PHYSICAL CHEMISTRY

THIRD EDITION

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PREFACE

BUNSEN is reported to have said, "Ein Chemiker, der kein Physiker ist, ist gar nichts." (A chemist, who is no physicist, is almost valueless.) If this were true sixty years ago, it is even more true to-day. The co-ordination of physics and chemistry, of which Ostwald laid the foundation, now forms the basis upon which chemistry is built. No one can study chemistry with profit unless he has a knowledge of those physical methods which have raised the subject from being a mere collection of facts to a science with a rational basis.

This book sets out to give an up-to-date outline of the results and methods of Physical Chemistry. Whilst it is not intended to be merely a "cram-book" for examinations, the standard to which it takes the subject is conveniently stated in terms of examinations. The book is suitable for students who are preparing for the Higher School Certificate and Intermediate Science Examinations of the various Universities, for University Scholarships, and for University Degrees up to Pass standard. It is realised that the first of these classes will not need to read the whole of the book, and accordingly a list of the paragraphs required for the Higher School Certificate is given. The wise teacher will use this as it is intended—merely as a recommendation. There is no need to emphasise the value of using one text-book for all the examinations enumerated above. The student gets to know the book, and can easily turn up any particular topic. This does not, of course, imply that the student should not augment his knowledge by reading some of the many monographs on various aspects of the subject; indeed, it is hoped that the reading of this book will stimulate him to read more widely, and to this end a list of books which are recommended for further reading is appended to each chapter.

Many students who take Chemistry in the various Public and University Examinations find this branch of the subject difficult because of their lack of knowledge of Physics. They are mainly those who take Chemistry, Botany and Zoology, and have left their Physics at the matriculation stage. For them this book is specially suited, as pains have been taken to make the Physics and Mathematics as simple as possible. Where any physical concept is introduced which is not likely to have been met with by a student

of this standard, it is fully explained. This may have entailed the use of some space, but such treatment is justified by the needs of a large class of students. The mathematics used is of the simplest consistent with the subject being an exact science.

Physical Chemistry naturally begins with the study of the atom. In this matter both Physics and Chemistry are on common ground: but so frequently does the chemist look upon this work as pure Physics, that the student must needs go to a text-book of Physics to learn about it. This necessity has been obviated in this book by commencing with an account of the methods used in deciding the structure of the atom. The knowledge thus gained is applied to the study of chemical combination by the electronic theory of valency. This is one of the most outstanding advances in Physical Chemistry of recent years, and has already brought about great changes in the presentation of the facts of Inorganic Chemistry.

All the topics usually dealt with under the heading of Physical Chemistry will be found in this book. It has been made as up to date as possible by the inclusion of recent work on the theory of complete dissociation, the hydrogen isotope, the physical determination of atomic weights, the extended theory of acids and bases, atomic transmutation, the neutron and positive electron, and other topics. A chapter on Photochemistry is included, and it is hoped that this brief account will be of use to students, as few books of this standard mention the subject. Finally, the methods employed in determining the structure of comparatively simple molecules are outlined. This advance in Physical Chemistry is the logical successor to the unravelling of the structure of the atom, and deserves a chapter in a book of this nature.

Summaries are appended to the chapters in the hope that they will assist in revision, for those readers who have to be examined in the subject. Many cross-references in the text enable any particular subject to be quickly traced. A selection of examples is also given. Some of these are descriptive, others are calculations, based, for the most part, on research work described in the various scientific journals.

The book is not intended to be a text-book of Practical Physical Chemistry, but, for the sake of completeness, suggestions for practical work are made at the end of each chapter, and brief outlines for conducting the experiments are given. Greater detail will be found in the text-books devoted to this branch, such as Findlay's *Practical Physical Chemistry* (Longmans), Fajans and Wust's *Practical Physical Chemistry*, translated by Topley (Methuen), and Sherwood Taylor's *Elementary Practical Physical Chemistry* (Oxford University Press), to quote a few.

PREFACE

I most gratefully acknowledge the help of the many sources I have used in the preparation of this book. It is impossible to mention all of them, as every book on the subject that I have read has left its impression upon my memory. All the books mentioned at the end of each chapter have been consulted. I must, however, mention the following, which have been particularly useful. Dr. J. Newton Friend's *Text-book of Physical Chemistry*, Volume I. (Griffin), has been frequently consulted on the properties of liquids, and other points, and has provided me with a considerable amount of data for the compilation of some of the tables. *A Treatise on Physical Chemistry* (Macmillan), edited by H. S. Taylor, has proved very useful on a great variety of topics. J. W. Mellor's *Comprehensive Treatise on Inorganic Chemistry*, Volume I. (Longmans), was consulted in connection with Chapter I., and particularly on the history of the liquefaction of gases. Professor S. Sugden's *The Parachor and Valency* (Routledge) gave me considerable help on the subject of atomic spectra, and many of the figures used in the tables of Chapter III. have been derived from this source. It also provided me with the greater part of my information on the Parachor, and the theory of singlet linkages. Professor N. V. Sidgwick's books, *The Electronic Theory of Valency* (Oxford) and *The Covalent Link in Chemistry* (Cornell University Press), have been most valuable in connection with Chapters IV. and XX. respectively. These books should be known by every student of Chemistry. Dr. Eggert's *Lehrbuch der Physikalischen Chemie*, which has now been translated by Dr. S. J. Gregg (Constable), has proved of very great value on many points, and particularly on Photochemistry. I have adopted Dr. Eggert's method of dealing with this subject in Chapter XIX. The *Annual Reports of the Progress of Chemistry* issued by the Chemical Society have been used freely. The books on Practical Physical Chemistry mentioned on the previous page have been used in connection with the experiments described at the ends of the chapters.

The following have kindly given their permission to reproduce diagrams, tables, etc. :—

Professor E. K. Rideal and the Chemical Society, for Plate V., from the *Annual Reports of the Progress of Chemistry*, 1931, p. 322.

Professor N. V. Sidgwick and the Cornell University Press, for Tables CIII., CIV., CXXII., CXXIII., from *The Covalent Link in Chemistry*.

Messrs. Routledge & Sons Ltd., for the use of data from Professor S. Sugden's *The Parachor and Valency* employed in Tables XV.–XX., and XXX.

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Messrs. Edward Arnold & Co., for Fig. 38, from Aston's *Mass Spectra and Isotopes*; for the use of data, on pp. 240 and 241, from Prof. J. B. Cohen's *Organic Chemistry for Advanced Students*, Vol. II.; and for Figs 86 and 202, based on Figs. 8 and 13 respectively of Dr. E. S. Hedges' *Chapters in Modern Inorganic and Theoretical Chemistry.*
Dr. P. M. S. Blackett, Messrs. G. Bell and Sons, for Plate II., from Andrade's *Structure of the Atom*, and Fig. 44 from the same source.
Messrs. Longmans, Green & Co. Ltd., for Table LVII., from Findlay's *The Phase Rule and its Applications.*
Messrs. D. Van Nostrand, for Fig. 173, from H. S. Taylor's *Treatise on Physical Chemistry.*
The Chemical Society for the Table of International Atomic Weights (1934), given on p. 754, and the data for several other tables taken from the *Journal of the Chemical Society.*
Dr. J. Newton Friend and Messrs. Charles Griffin & Co. Ltd., for the use of data on pp. 259 and 260, and Table LXVIII., from Dr. Friend's *Text-book of Physical Chemistry*, Volume I.

The publishers have allowed me to use certain blocks of illustrations appearing in other of their books.

I must tender my most sincere thanks to my Publisher's Science Editor, who kindly read the work in the manuscript stage, and pointed out numerous improvements. Without his help the book would have been much impoverished. He has also read the proofs, and supervised the preparation of the blocks. I am also very grateful to Dr. L. A. Woodward, who read the work in manuscript and gave many valuable criticisms and suggestions. I have made considerable use of the Library of the Chemical Society, and my best thanks are due to the Librarian, Mr. F. W. Clifford, and the Staff for the help they have always been ready to give.

Finally, the Publishers have done all in their power to make the work entailed in the preparation of a book like this as light as possible for the author, and have always sought to carry out my wishes to the smallest detail.

June, 1934. A. J. M.

PREFACE TO THE SECOND EDITION

THE need for a further reprinting of this book has provided the opportunity of bringing it up-to-date. During the last five years there has been a considerable advance in our knowledge of the structure of the atomic nucleus, and it is now generally accepted that the neutron is a constituent of it. This change of view has made it necessary to rewrite parts of Chapter II. and to make alterations in various other parts of the book. The electronic theory of valency has also been extended during recent years and space has been found to mention the theory of resonance as an explanation of the covalency of hydrogen.

It is hoped that the usefulness of the book has been increased by the inclusion of tables of logarithms.

I take this opportunity of thanking all those who have pointed out errors in the first edition, and who have offered constructive criticism.

April, 1939. A. J. M.

PREFACE TO THE THIRD EDITION

OUR knowledge of the structure of the atom, and with it that of the theory of valency and chemical combination, has increased so much within recent years that it has become necessary to extend and revise the portions of this book devoted to these topics. At the same time the remainder of the book has been corrected and brought up-to-date. The incorporation of this new matter has involved the complete resetting of large portions of the book, and the preparation of new blocks.

I have much pleasure in acknowledging my indebtedness to those readers who have written to suggest improvements.

July, 1947. A. J. M.

PUBLISHER'S NOTE TO THE THIRD EDITION

To maintain uniformity with previous editions, and to avoid the long delay which would ensue from renumbering the pages of the entire book, the following page numbers appear:

92a, 92b, 92c, 92d, 110a, 110b, 180a, 180b, 180c, 180d,

A SUGGESTED COURSE FOR HIGHER SCHOOL CERTIFICATE EXAMINATIONS

The course outlined below is considered to be suitable for those students preparing for the Higher School Certificate or Intermediate Science Examinations. Those who intend to enter for University Scholarships would be well advised to read the complete book.

Chapter I.—§ 1–13.

Chapter II.—§ 14–36, 38–40, 42.

Chapter IV.—§ 58–68.

Chapter V.—§ 69–82.

Chapter VI.—§ 83–86, 89–93, 96–104, 106–110, 113–118.

Chapter VII.—§ 120, 125, 132–139, 144, 146–147, 149, 150.

Chapter VIII.—§ 151–169.

Chapter IX.—§ 172–176.

Chapter X.—§ 179–182, 184–221.

Chapter XI.—§ 222–246.

Chapter XII.—§ 247–267.

Chapter XIII.—§ 271–289.

Chapter XIV.—§ 290–299.

Chapter XV.—§ 300–309.

Chapter XVI.—§ 312–324. The thermodynamic derivations may be omitted by non-mathematical students, but the results should be known.

Chapter XVII.—§ 327–347.

Chapter XVIII.—§ 348–357.

CONTENTS

[1] The figures refer to the numbers of sections.

ABBREVIATIONS

The abbreviations used throughout this book are those adopted by the Chemical Society in the *Journal*, with the exception of the abbreviation for *gramme*, which is given as *gm.*

LIST OF PLATES

PHYSICAL CHEMISTRY

CHAPTER I

LAWS OF CHEMICAL COMBINATION

1. The Law of Conservation of Matter.—This law, which is the basis of all quantitative work in chemistry, was first stated by Lavoisier in 1774, although the belief in its truth was current much earlier amongst the Greek philosophers.

The law states that *the total amount of matter in the universe is unaltered, whatever changes take place in its distribution.* The Greeks merely gave this as an opinion, or a belief; their views were not founded on any experiment. Lavoisier, however, came to his conclusion as the result of experiment, and he stated the law in the words: "Nothing can be created, and in every process there is just as much substance present before and after the process has taken place. There is only a change in the form of the matter."

FIG. 1.—Landolt's Tube.

Experimental proof of the Law of Conservation of Matter is difficult. By many chemists the truth of the law was regarded as self-evident, since so much quantitative work had been based on it, and it had always turned out correct within the limits of experimental error. The law was subjected to an exhaustive test by Landolt, whose results were published in 1906, and Heydweiller (1901).

It is clear that to test the law, reactions must be carried out in sealed tubes so that none of the products of the reaction escape. Heydweiller (*Ann. Physik.*, 1901, (IV.), **5**, 394) found slight losses in weight when reactions were carried out under these conditions, and Landolt (*Z. physikal. Chem.*, 1906, **55**, 589) set to work to discover to what these losses were due. The simplest form of apparatus employed by him was an H-tube, as shown in Fig. 1, in which the two reactants could be placed in either leg. On inverting the tube, the two substances mixed and reaction took place. If the Law of Conservation of Matter is valid, there should be no difference in the weight of the tube before and after the mixing.

Fifteen different reactions were used, amongst which were the following:—

(1) Silver sulphate solution in one limb, and ferrous sulphate in the other; on mixing metallic silver was deposited.
(2) Hydriodic acid and iodic acid, which on mixing gave a precipitate of iodine.
(3) Sodium sulphite and iodine, which reacted giving sodium iodide and sodium sulphate.
(4) Potassium hydroxide solution and chloral hydrate, which gave an emulsion of chloroform.

In carrying out an experiment, one tube was counterbalanced against another exactly similar tube. One tube was then inverted, replaced on the balance, and the change in weight noted. The other tube was then inverted, and replaced on the balance, and the change in weight found. The process was repeated several times, and in almost every case a diminution in weight was found.

These losses in weight were found to be due to: (*a*) a slight heat evolution in the reaction which removed some of the moisture which is always present on a glass surface; it took some time for this moisture to return; (*b*) the heat evolution caused a slight expansion of the vessel, which did not regain its original volume at once.

Both these effects would tend to reduce the weight or apparent weight of the containing vessel, giving rise to the apparent loss in weight. It has been shown that, for gaseous reactions, a loss in weight may be occasioned by the permeability of the glass vessel to certain gases. When the surface is coated with paraffin wax, this effect is eliminated.

The two effects mentioned above could be eliminated if the reaction vessel were allowed to stand long enough after the reaction had taken place, and Landolt found that when this was done the original weight was regained to within 1 part in 10,000,000, an error quite within the limits of the experiment. For these reactions, then, the law may be taken as valid.

However, all the reactions studied take place quietly. There is no great evolution of light or heat. The difficulties encountered in the study of vigorous reactions, with a view to proving that the Law of Conservation of Matter holds for them, are so great, that it is not known whether they do obey the law. Our modern idea of radiation and matter leads to the view that they would not obey the law. The emission of radiation, such as light and heat, is accompanied by a loss of mass, which is equal to $\frac{E}{c^2}$, where E is the energy radiated

and c the velocity of light. The sun, which is continually radiating, is all the time losing part of its matter. Actually, in all chemical reactions, radiation of some sort is emitted, and consequently the law of conservation of matter can no longer be regarded as an exact law. In ordinary work, however, the amount of radiation emitted is so small as to make any correction in the application of the law quite negligible, although in the most energetic reactions a change of 1 part in 10^8 might be found.

There is little doubt that a true conservation of mass and energy, taken together, does exist.

2. The Law of Constant Proportions.—Proust, as a result of his analyses of compounds, was able, in 1799, to make the generalisation that "*when combination takes place between elements, it is in definite proportions by weight, so that the composition of a pure chemical compound is independent of the method by which it is prepared.*"

This Law, which seems to us self-evident, actually proved to be the centre of a controversy at the beginning of the nineteenth century, between Proust, and the French chemist Berthollet. The latter believed that the composition of a compound was variable, and supported his view by several pieces of experimental evidence, all of which, as Proust was able to show, did not actually amount to any violation of the law. Berthollet said that when lead is heated in air it gradually takes up oxygen, and its colour changes from grey, through yellow to red. There were thus a large number of compounds of lead and oxygen, but no definite proportion of lead and oxygen in them, for the colour changed insensibly from one to the other. Proust was able to show that actually there was a series of oxides of lead, each of which has a fixed and definite composition, and that the colour changes gradually when lead takes up oxygen from the air because the relative proportions of these different oxides are changing.

Berthollet also stated that when mercury dissolves in nitric acid, it takes up the acid in various proportions continuously from a minimum amount, when the mercury is converted into a mercurous salt, to a maximum, when it gives a mercuric salt. Proust showed that there were only two mercury nitrates, a mercurous and a mercuric salt, and that the intermediate substances were merely mixtures of these two.

Numerous other objections were raised by Berthollet, whose one aim at this time seems to have been to overthrow this Law by every means in his power. In every case, however, Proust was able to bring forward evidence in favour of the Law, although this was often a difficult matter. If this controversy was bitter, it did at least promote chemical investigation, and a great increase in

chemical knowledge was made at this time largely as a result of it.

The Law has been proved within the limits of experimental error by the work of Stas, who prepared compounds in several different ways, and showed that their composition was the same to within 1 part in 100,000.

No error in any quantitative analysis has been traced to a failure of the Law, so that, although it has not been directly verified for all substances, a task of such magnitude that it could not be completed, this indirect evidence places its accuracy, as an experimental law, quite beyond doubt.

The converse of the Law of Constant Proportions is not true. If it is found that two compounds have the same composition by weight, it does not necessarily follow that they are one and the same substance. This is due to the existence of isomerides, *i.e.*, substances possessing identity of chemical composition, yet having different properties. A well-known example of this is the isomerism shown by many organic substances, such as urea, $CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$, and ammonium cyanate, NH_4CNO. Both these substances have the same molecular formula, N_2H_4CO, and yet they are entirely different in their properties. Ethyl ether, $(C_2H_5)_2O$, and butyl alcohol, C_4H_9OH, are further examples of isomerides. Chemical composition does not therefore uniquely determine a chemical compound.

It should also be noted that it is possible to find two or more definite chemical compounds with identical *chemical* properties, yet differing in *physical* properties and in chemical composition. Thus, lead chloride prepared from metallic lead which has had its origin in the disintegration of uranium minerals, differs in composition from that prepared from lead from thorium minerals. It has identical properties, but different composition. The reason for the difference lies in the fact that the lead from the two sources differs in atomic weight. The atomic weight of ordinary lead is 207·2, whilst that from certain radioactive sources is 208. It is clear that the lead chloride prepared from each of these specimens will have different compositions, although no outward chemical difference can be discovered between them. Actually almost every element is made up of a mixture of atoms of different atomic weights (§ 35) Although these atoms differ as regards weight they do not differ at all chemically, and so chemical tests fail to distinguish between them Such atoms are called isotopes. Chlorine gas, as ordinarily prepared, consists of a mixture of atoms of atomic weights 35 and 37.

If these could be separated, and then combined with sodium, they would both form common salt, which would give all the chemical tests for this compound, and both specimens would be chemically indistinguishable from each other. Yet it is clear they would not have the same composition. In practice the ordinary elements always contain the same isotopes in the same proportions, and so compounds always have the same composition, whenever and however they are prepared. In order that the Law may be applied, it is necessary to distinguish carefully between compounds formed from different isotopes.

3. The Law of Multiple Proportions.—This Law was stated by Dalton in 1803, and may be put as follows :—

When two elements A and B combine to form more than one compound, the weights of A, which combine with a fixed weight of B, are in the proportion of small whole numbers.

There is little doubt that Dalton had been working on the atomic theory, and saw that some such law must necessarily be true (§ 9). He found in his experiments on the hydrocarbons marsh gas (methane) and olefiant gas (ethylene), and on the oxides of carbon, some experimental evidence for this view. It is certain that no man of science without an idea of what result to expect would have propounded the Law of Multiple Proportions from the numerical results of Dalton's experiments. The experiments were very crude, and the results far from accurate. Only a person who expected the Law to be true would be able to see the truth of it from Dalton's figures.

Numerous experiments since, however, have shown the truth of the Law. Analyses by Berzelius were considerably more accurate than those of Dalton and provided sufficient experimental evidence. The analysis of three of the oxides of nitrogen has been carried out by different observers and the results are given below :—

Nitrous oxide (Guye and Bogdan, 1904), N : O = 1·75100 : 1.

Nitric oxide (Gray, 1905), N : O = 0·87563 : 1.

Nitrogen tetroxide (Guye and Drouginine, 1910), N : O = 0·43782 : 1.

The numbers expressing the amount of nitrogen combining with 1 part of oxygen are in the proportion,

$$1{\cdot}75100 : 0{\cdot}87563 : 0{\cdot}43782,$$

i.e.,
$$3{\cdot}9994 : 2 : 1,$$

or
$$4 : 2 : 1.$$

Similar remarks apply concerning the exactness of this Law as were made regarding that of the Law of Constant Proportions. The existence of isotopes causes similar discrepancies here, unless the

same isotope or mixture of isotopes is used throughout the preparation of a series of compounds. This difficulty is only likely to arise with compounds of hydrogen (§ 40, 41) and possibly lead.

4. The Law of Equivalent Proportions, and the Law of Reciprocal Proportions.—The fact that combination between substances takes place between definite weights of them appears to have been recognised by some of the alchemists, particularly by one Al Jildaki, who lived in the fourteenth century. Cavendish, however, was the first to recognise that substances combined together in the proportion of their equivalent weights. Cavendish (1766) first mentioned the word equivalent when dealing with the neutralisation of lime by an acid. He found the weight of potash which would combine with a given weight of acid, and the weight of lime which would neutralise the same weight of acid. He said that these two weights were equivalent.

The analysis of a number of salts was carried out by Wenzel (1777), but he did not arrive at the Law of Equivalents. The first to note the relationship was Richter in 1792–94. He gave the Law of Reciprocal Proportions, which is a special case of the more general Law of Equivalent Proportions. The Law of Reciprocal Proportions states that "*the weights of two or more substances which separately react chemically with identical weights of a third are also the weights which react with each other, or simple multiples of them.*"

The following example may be taken to illustrate the Law :—

(1) Sodium combines with hydrogen, forming sodium hydride ; 23 gms. of sodium combine with 1 gm. of hydrogen.

(2) Sodium combines with oxygen to form sodium oxide ; 23 gms. of sodium combine with 8 gms. of oxygen.

(3) Hydrogen combines with oxygen to form water ; 1 gm. of hydrogen combines with 8 gms. of oxygen

Here there are two substances (they happen to be elements in this case) combining with the same weight of a third. If the Law of Reciprocal Proportions is correct it would be expected that the weights of the two elements would be those in which they would combine with each other, and that is indeed the case.

It will be seen that as it stands this Law is of limited applicability, for there are comparatively few substances which, combining with a third, will combine with each other. The fact that they do both combine with the third element means that they must be similar in nature, and combination between similar substances is not to be expected.

The Law could, however, be applied through a chain of substances, and in this way we should arrive at a series of numbers which express the weights with which the different elements would

combine with each other. These weights are known as the equivalents of the elements or compounds.

It was formerly usual to take hydrogen as the standard element, because no element was known which had a smaller equivalent; but for various reasons to be stated later, it is now customary to take oxygen as the standard (§ 5).

The *equivalent* of a substance is therefore defined as the *weight of it which will combine with or displace* 8 *parts by weight of oxygen.*

The Law of Equivalents states that *substances combine together in the ratio of their equivalents.*

The most recent values for the equivalents of hydrogen, chlorine, and silver are 1·0078, 35·457 and 107·880 respectively. These numbers are of great importance as they are fundamental for the determination of other equivalents. It is not always possible to make an element combine with hydrogen, or even with oxygen, but there are few elements which will not combine with chlorine. Since the equivalent of chlorine, referred to oxygen, is known, it is possible to find the equivalent of a substance by analysing its compound with chlorine. This method, of course, makes use of the Law of Equivalents.

The equivalents of most elements are based on the equivalent of silver, since the chlorides of most elements can be prepared in a pure condition, and chlorine can be determined as silver chloride with great accuracy.

5. The Oxygen Standard.—Dalton chose the atom of hydrogen as the standard upon which to base the atomic weights (§ 11) of the other elements. He did this because the hydrogen atom was the lightest.

It so happened that the atomic weights of many other elements determined on this standard came out to be very nearly whole numbers. The number of them which did so was much greater than that indicated by probability, and so Prout, who, by the way, was one of the pioneers of physiological chemistry, considered that they ought to be whole numbers. So he put forward his famous hypothesis that the atomic weights of all elements are multiples of those of hydrogen. This caused the view that hydrogen should be taken as the standard to be held even more strongly.

If Prout's hypothesis were correct, it was considered that it ought to be possible to prove by experiment that the atomic weights of all elements were whole numbers and not merely nearly whole numbers, but all attempts to bring the elements into this scheme failed. The elements copper and chlorine, with atomic weights 63·57 and 35·46 respectively, proved particularly recalcitrant in this respect. The inability of the theory to cover these cases proved its downfall.

There was, however, much more truth in Prout's hypothesis than was at this time imagined, and in the light of the modern view of atomic structure it has again come into its own. That is another story, and must be taken up in the next chapter (§ 35, 37).

For practical purposes it was found convenient to take oxygen with the value 16·000 as the standard of atomic weights. The reasons for this step were :—

(1) It is much more easy to obtain compounds of elements with oxygen than with hydrogen, particularly in the case of the metals. At the time when atomic weights were being determined with accuracy, the preparation and analysis of hydrides was a difficult matter. As it was, on the basis of hydrogen = 1, the atomic weights of elements frequently had to be determined with oxygen as an intermediary, and this meant that every time the atomic weight of oxygen was redetermined, many other atomic weights had to be recalculated. With the atomic weight of oxygen fixed, this would be unnecessary.

(2) The atom of hydrogen is very light, and in making comparisons experimental errors are magnified.

At the time when this work was done nothing was known of isotopes, but it has been found that the masses of isotopes come out to be more nearly whole numbers on the oxygen scale. It is now known that oxygen itself is a mixture of isotopes of masses 16, 17 and 18, the proportion of the last two being very small. For chemical purposes the naturally occurring mixture is taken as the standard, but the 16 isotope is the standard used in the mass spectrograph method for determining atomic weights (§ 38). The ratio of a mass on the standard $O^{16}=16$ to that on the other is $1{\cdot}00027 \pm 0{\cdot}00002$, according to the most recent determinations. The discovery of the hydrogen isotope, H^2, is also of importance in this connection (§ 40).

6. The Determination of Equivalents.—The accurate determination of equivalents is a matter of great importance, since the atomic weight of an element is nearly always derived from this figure. If the atomic weight of the element on the hydrogen scale is a, and the valency is v, one atom of the element combines with v atoms of hydrogen. But, one atom of the element weighs a units, compared with hydrogen. Hence a grams of the element combine with v grams of hydrogen. The equivalent is, this, $\frac{a}{v}$. The atomic weight of an element and its equivalent are therefore connected by the relationship,

$$\text{equivalent} \times \text{valency} = \text{atomic weight}.$$

The atomic weight is always some simple multiple of the equivalent.

During last century the most accurate work in the determination of equivalents was done by Stas, the master of quantitative analysis. Stas commenced work by studying the action of heat on potassium chlorate. He found the loss in weight that took place when a given weight of potassium chlorate was heated until it gave off no more oxygen. He knew that the compound contained six equivalents of oxygen, so he could determine the equivalent of potassium chloride. He found this to be 74·59 (O = 8). By finding the weight of silver chloride precipitated by a given weight of potassium chloride he found the equivalent of silver chloride to be 143·37. The combination of a known weight of silver with chlorine gave him the equivalent of silver, 107·93. Knowing this, he obtained from his other figures the values for potassium and chlorine.

The results of his analyses were extraordinarily accurate, but unfortunately there were two systematic errors. The first was due to the fact that the potassium chlorate contained a small quantity of chloride, and the second the fact that a small quantity of potassium chloride is always carried down by silver chloride when precipitated by silver nitrate, and this impurity cannot be removed by washing. The work of Edgar on the direct determination of the equivalent of chlorine showed the existence of this error.

Some examples of the extreme care which has to be taken to obtain an accurate value for the equivalent will be given later when we consider some of the classical experiments that have been carried out with this end in view (§ 13).

The determination of atomic weights and of equivalents is, however, fast becoming the task of the physicist rather than of the chemist, for results of as great a degree of accuracy can be obtained by physical methods as by chemical ones. This will be more fully realised after reading the next chapter (§ 38).

It will be of value to summarise, at this point, the simpler methods that are available in the laboratory for the determination of equivalents. Although these yield results of only moderate accuracy, they form the nucleus of the more elaborate methods.

(1) The determination of the volume of hydrogen that is evolved by the use of a given weight of metal when treated with an acid, or sometimes an alkali. This method is now never used for accurate work.

(2) The determination of the weight of the substance which will combine with 8 gms. of oxygen.

This may be done either by making a known weight of the element into its oxide, and weighing the oxide, or by starting with a known weight of oxide, reducing it to the element, and weighing the element.

(3) Determination of the weight of silver necessary to precipitate a known weight of the chloride of the element.

Thus, to determine the equivalent of sodium, sodium chloride is taken. A known weight of the salt is dissolved in water, and silver nitrate solution added until precipitation is complete. The precipitated silver chloride is filtered off through a quantitative filter-paper, or a weighed Gooch crucible, washed, dried, ignited (if a paper is used), and weighed. From the weight of the silver chloride the weight of chlorine in the salt is obtained. The equivalent is calculated by finding the weight of metal combining with 35·457 gms. of chlorine.

Alternatively, silver may be taken as the standard, and the weight of silver required to precipitate a known weight of the chloride may be calculated. The equivalent of the compound is that weight of it which is precipitated by 107·880 gms. of silver. The equivalent of the metal is found by subtracting the equivalent of the chlorine present from the equivalent of the chloride.

This method is the one now most frequently used. As an example, the work of Briscoe, Kikuchi and Peel (*Proc. Roy. Soc.*, 1931, *A*, **133**, 440) on the determination of the equivalent of thallium may be quoted. Thallous chloride was carefully purified, and a solution containing a known weight of it was prepared. Excess of silver nitrate solution was added, and, after standing, the supernatant liquid was decanted, evaporated to a small bulk, and the silver in excess was determined by titration with $N/1,000$-thiocyanate. One series of results is given in the table below :—

TABLE I.—EQUIVALENT OF THALLIUM

Wt of TlCl gms.	Wt. of Ag gms.	TlCl : Ag.	At. wt. of Tl ∴ Equivalent
10·04965	4·52210	2·22234	204·29
11·55090	5·19723	2·22251	204·31
10·60756	4·77211	2·22282	204·34
9·91726	4·46146	2·22288	204·35
9·53722	4·29023	2·22300	204·36
11·88154	5·34523	2·22283	204·34
		Mean	204·33

The figures in column 4 are both the equivalent and the atomic weight of the element as, in the thallous state, the element is univalent.

(4) By displacing another element from combination.

Take, as an example, the determination of the equivalent of copper by adding a known weight of zinc to copper sulphate solution. Copper is deposited and the zinc dissolves. The precipitated copper is filtered off, dried, and weighed. The equivalent of zinc must be known, the calculation depending on the law of equivalents (§ 4) :—

$$\frac{\text{wt. of copper deposited}}{\text{wt. of zinc dissolved}} = \frac{\text{equivalent of copper}}{\text{equivalent of zinc}}.$$

(5) By conversion into another compound.

To find the equivalent of nitrogen, potassium chloride may be converted quantitatively into potassium nitrate. All the equivalents are known with the exception of that required. The equivalent of a compound is the sum of the equivalents of its constituent elements.

(6) The equivalent of a compound can frequently be found by volumetric methods.

Thus one equivalent of ammonium thiocyanate reacts with one of silver nitrate. A solution containing a known weight of ammonium thiocyanate is titrated against a standard solution of silver nitrate by the usual method. The weight of ammonium thiocyanate combining with the equivalent weight of silver nitrate can then be readily calculated.

An element may, of course, have more than one equivalent. If the valency of an element is variable, its equivalent will be variable also, since the two are connected by the relationship mentioned above.

7. The Law of Combining Volumes.—Gay-Lussac (1808), on the basis of numerous experiments carried out by himself, and also in conjunction with Humboldt, arrived at the conclusion that *when gases combine they do so in volumes which bear a simple relationship to each other, and to that of the product if that is also gaseous.*

The Law was at first regarded as being strictly true, for accurate working with gases is quite a modern development. More recently it has been found that the Law is only approximately true. Thus, the experiments of Morley on the combining volumes of hydrogen and oxygen showed that the ratio is 2·00269 : 1, instead of exactly 2 : 1, the difference not being accounted for as experimental error. Numerous other experiments show that the combining volumes *approximate* to whole numbers. The reason for the deviation is the fact that no gas is ideal and obeys the gas laws. If Boyle's and

Charles' Laws were obeyed it can be shown that Gay-Lussac's Law would be strictly true. Since all gases obey Boyle's Law more closely at low pressures, it follows that the law of combining volumes will more nearly express the facts when the gases are in this condition (see also Chapter V., § 82).

As an elementary example of the verification of this Law the volumetric composition of any compound gas will serve, and the methods of determination should be revised here.

8. The Ancient Atomic Theory.—The idea that matter is not indefinitely divisible, but is made up of minute indivisible particles, is not modern. That matter was made up of atoms was suspected by the Greeks—it cannot be said that it was more than a suspicion, for there was no experimental proof of their view. Some of the philosophers assumed an atomic theory because it explained the phenomenon of the mixture of liquids, which is difficult to conceive without a belief in the discrete nature of matter. This view of the constitution of matter was held by Leucippus and Democritus, four centuries B.C., and the idea was more fully developed by Lucretius. The conclusions of Lucretius are of considerable interest, for, as has been pointed out by Tait, and Young, they are very like those actually put forward by Dalton more than two thousand years later. They were :—

(1) Atoms have different shapes : but the number of shapes is finite, and there is an infinite number of atoms of each shape.

(2) Nothing whose nature is apparent to sense consists of one kind of atom only.

(3) The atoms move through space at a greater speed than that of sunlight.

The atomic nature of matter was tacitly assumed by such men as Bacon, Boyle, Hooke and Newton. But any considerable increase in our knowledge of the nature of matter was held up through the lack of a clear idea of the nature of elements. To the alchemists there were four elements : earth, air, fire and water. These, indeed, represented the three states of matter, solid, gas, and liquid, with the addition of fire, which, as it was not in the slightest degree understood, was classified as an element. The conception of the term "element" was, however, much more complex than is indicated by this statement. The majority of the alchemists believed in the Aristotelian continuum of the four elements.

Boyle was the first to give any precise definition of the term "element." He defined it as a substance which itself was not capable of further separation, but which could be obtained from a compound. In these days we find it necessary to make some modification in this definition, which, however, was still quite

satisfactory until the beginning of this century. It is now rather difficult to define an element, for almost all elements have been "decomposed." By bombarding elements with rapidly moving protons and neutrons it has been found possible to break them down into simpler ones. For details of this, see Chapter II., § 42.

We may now define an element as *a substance which cannot be broken down into something simpler by the ordinary chemical methods*, though, of course, this definition is vague, since it does not define what ordinary chemical methods are. Although it is difficult to give a definition, yet we have a physical method of finding out whether a substance is an element or not quite definitely, making use of the X-ray spectrum.[1]

This uncertainty about the definition of the element is quite a modern development, dating from the time of the discovery of radioactive disintegration. It was certainly unknown in the eighteenth and nineteenth century, and at the time that Dalton lived, the idea of an element was quite fixed, as also was that of the atomic nature of matter. Two Irish chemists who preceded Dalton, Bryan Higgins (1737–1820) and William Higgins (1769–1825) got so far as to suggest that chemical combination was due to the union of single ultimate particles of the combining substances, but made the false assumption that the ultimate particles of all substances had the same weight.

There can be no doubt that the time was ripe for the atomic theory; many experimental facts were leading to this inevitable conclusion. It was left to Dalton (1766–1844) to propound the theory—the most far-reaching in its consequences that chemistry has ever known.

9. Dalton's Atomic Theory.—Dalton's views may be summarised in the following terms :—

(1) Elements are made up of atoms, which are indestructible. All atoms of the same element have the same weight, and are similar in size and shape.

(2) Compound atoms are formed by the union of elementary atoms in simple proportions.

It is surprising how closely related these statements are to the views of Lucretius.[2] Thus, the first statement of Lucretius, when modified to suit the Dalton theory, reads :—

[1] A good modern definition of an element is "a substance which consists wholly of atoms having the same nuclear charge." This definition calls a mixture of isotopes an element, which is common usage. The X-ray spectrum depends on the intensity of binding of the K-electrons, which is a function of the nuclear charge. This note will be more clearly understood after reading Chapters II and III.

[2] S. Young. "Stoichiometry," p. 8. (Longmans, 1908.)

(1) Atoms have different weights, but the number of weights is finite, and there is an infinite number of atoms of each weight.

All that is required is the substitution of the word weight for shape.

(2) Chemical elements consist of one kind of atom only.

(3) Actually the atoms move with a speed very much less than that of light. Dalton did not investigate the speeds of atoms, but the velocities of molecules of gases have since been determined by the aid of the kinetic theory (see § 75, where a table of molecular velocities is given). The most rapidly moving atom moves (at N.T.P.) with a speed no greater than that of a rifle bullet.

There seems to be no doubt that Dalton arrived at his theory on purely physical lines, and that he was very much influenced by Newton. Dalton probably had these ideas in his mind for some years before making them public, and he frequently mentioned the theory, or at least isolated points in it, in lectures.

The theory explained in a very convincing way the various laws of chemical combination that had already been formulated.

The fact that compounds always contain their constituent elements combined in fixed proportions follows, since combination can only take place between atoms, and these have definite weights.

If two elements, A and B, combine to form more than one compound, the molecules of the compounds must be made up of 1 atom of A + 1 atom of B, 1 atom of A + 2 atoms of B, 1 atom of A + 3 atoms of B, 2 atoms of A + 1 atom of B, etc. Since the mass of an atom of A is constant, as is also that of an atom of B, the compounds must obey the Law of Multiple Proportions.

When it came to Gay-Lussac's Law of Combining Volumes, however, Dalton's theory experienced difficulties. It was known, for example, that one volume of hydrogen combined with one volume of chlorine to form two volumes of hydrogen chloride. Dalton's theory postulated that combination took place between simply related numbers of atoms, and that in all probability, in this case, it was between single atoms. Berzelius indeed believed, as a result of combining Dalton's theory with Gay-Lussac's Law, that equal volumes of gases under the same conditions of temperature and pressure contained an equal number of atoms. On applying this hypothesis to the data we have before us, we see that it leads to the conclusion that one atom of hydrogen combines with one atom of chlorine to form two "atoms" of hydrogen chloride. The conception of an atom necessitated the possibility of obtaining a single "atom" of hydrogen chloride, and hence this single "atom" would contain half an atom of hydrogen and half an atom of chlorine. This meant that the atoms must be divisible into two halves, and

this was in direct contradiction to Dalton's statement that the atom was indivisible, a statement upon which he always laid great emphasis. Instead of looking for the error, however, in the assumption that equal volumes of gases contain the same number of atoms, he made the statement that gases do not combine exactly in simple proportions, and that whenever figures were obtained which agreed with that result, they were due to experimental error—a most remarkable thing to say in face of all the evidence. The correct interpretation of the matter was given by Avogadro, who pointed out the difference between atoms and molecules, and put forward his famous Hypothesis (1811). The latter was, however, disregarded until the middle of the century, and until this time the whole question remained in considerable confusion. When Avogadro's Hypothesis was accepted, the molecules of elementary gases were assumed to be diatomic.

10. Avogadro's Hypothesis.—It must be emphasised that Dalton's view of the atom was that it was the smallest particle of a substance that could exist, irrespective of whether the substance was an element or a compound. It was quite usual for Dalton to talk of an atom of a compound. Avogadro, however, recognised that the smallest particle of a compound could actually be further subdivided into its component atoms, and the term molecule was applied to the smallest particle of a compound that retained the chemical properties of the compound. *The molecular weight of a compound is the sum of the atomic weights of its constituent atoms.*

Avogadro, therefore, stated that "*equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules.*" The same hypothesis was put forward independently by Ampère a short while later.

This hypothesis was, at that time, incapable of direct experimental proof.

Avogadro's Hypothesis was not generally accepted until some forty-seven years later, when Cannizzaro revived it. Its fall into abeyance was due to the fact that the idea of the distinction between atom and molecule was not fully grasped. The Hypothesis has now become so much a part of our working stock in connection with gases that we do not stop to think whether it is true or not. It has shown that the common elementary gases are diatomic, and has provided a means of determining the atomic weights of the gaseous elements, which atomic weights are confirmed by many other methods. It is not, however, strictly true, for as in the Law of Volumes, upon which it depends, there are deviations due to the fact that no gas is ideal. The account which has to be taken of these deviations is fully explained on p. 208 (§ 82).

11. Methods of Determining Atomic Weights.—The atomic weight of an element was defined as the ratio of the weight of one atom of the element to that of an atom of hydrogen, though now it is usual to base atomic weights on the oxygen standard, and the definition then becomes *the ratio of the weight of an atom of the element to one-sixteenth of the weight of an atom of oxygen.*

At one time the atomic weight of an element was regarded as one of its most important constants, and particularly after the advent of the Periodic Law (§ 11, *d*) the atomic weight was supposed to be the factor determining the properties of an element. It is now known that it is not the atomic weight that is the important thing about an element, but the atomic number. The atomic number is defined as the numerical value of the net nuclear charge of the atom of the element, reckoned in units of positive charge equal in magnitude to the electronic charge (see § 34). This is the number of the element in the series of elements written in the order of the periodic table, taking account of the missing elements (*i.e.*, ascending order of atomic weight with certain departures indicated by the properties of the elements). Also, the atomic weight of an " element " is not necessarily a constant. Ordinary " elements " consist of a mixture of isotopes, *i.e.*, elements with identical chemical properties but different atomic weights (§ 35). It is true that the composition of these isotopic mixtures is always the same when the elements are prepared in the usual way, and the atomic weight will therefore appear to be a constant; but there is the likelihood that the composition of the mixture may alter with the source of the element, and then the atomic weight would differ from that usually determined. In fact, examples are known where the atomic weight of an element determined from some mineral source depends upon the age of the mineral, the composition of the isotopic mixture of atoms being different.

The atomic weight, then, can no longer be regarded as a fundamental constant of an element, and although much work has been done on the accurate determination of atomic weights, this has to a certain extent been wasted, since atomic weights have not the significance originally assigned to them. On the other hand, such accurate determinations led to the improvement of analytical methods. An accurate knowledge of atomic weights is, moreover, essential in the quantitative analyses on which the results of most chemical investigations depend.

We can only consider here the fundamental principles at the basis of atomic weight determinations. Much of the theory of the different processes employed is more fully dealt with in other parts of the book.

1. Gaseous Elements.—The atomic weight of a gaseous element (with the exception, of course, of hydrogen) is obtained from the relationship

$$\text{vapour density} = \text{molecular weight} /2.$$

Common elementary gases are all diatomic ; the exceptions are the inert gases. Hence, if the molecular weight is known, the atomic weight is found by dividing by two.

The relationship quoted above depends upon the validity of Avogadro's Hypothesis. Strictly, the Hypothesis only holds for ideal gases, and no gas is perfect. Gases do, however, approach ideality at low pressures, and so, the lower the pressure, the more nearly true is Avogadro's Hypothesis and the above relationship. The correction necessary for ordinary gases is explained in full on p. 208, § 82. The student is recommended, however, not to take it into account at this point, but to assume that Avogadro's Hypothesis is correct.

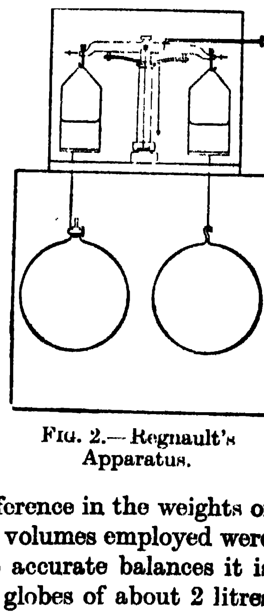


Fig. 2.—Regnault's Apparatus.

The method requires, then, a determination of the density of the gas. The exact determination of the density of a gas can be carried out in three ways :—

(a) *Regnault's Method.*—This consists simply of weighing a known volume of the gas under definite conditions of temperature and pressure. Regnault used large glass globes which were first evacuated, then filled with the gas, the difference in the weights of the globe giving the weight of the gas. The volumes employed were about 50 litres, but in these days of more accurate balances it is found much more convenient to use small globes of about 2 litres capacity, or even less.

The globe, of which the volume must be known, must first of all be very carefully dried. This is done by repeatedly filling the globe with air dried over phosphorus pentoxide, and then with the pure dry gas under investigation. The vessel is then completely evacuated. The purpose of this process is to replace any film of moisture on the inside of the glass globe with a film of the gas under examination. The globe is then hung from the beam of a balance and counterpoised by a similar globe, together with a few weights. This is to compensate for the film of moisture which is always to be

found on the outside of the glass globe, and also for changes in pressure and temperature in the neighbourhood. The vessel is then filled with gas at a known pressure, usually near 760 mm., and at a known temperature, usually 0° C. It is then weighed again, the additional weights placed on the side of the counterpoising globe being approximately equal to the weight of the gas.

Corrections now have to be made for buoyancy. The vessel, first evacuated, and then filled with a gas at atmospheric pressure, expands a little. When a vessel is weighed in air, the weight obtained is the actual weight of the vessel *in vacuo* less the weight of air displaced. The vessel when full of gas displaces more air than when it is evacuated, and consequently an addition will have to be made to the weight determined. This will be equal to the difference in volume of the globe, multiplied by the weight of 1 c.c. of air under the laboratory conditions.

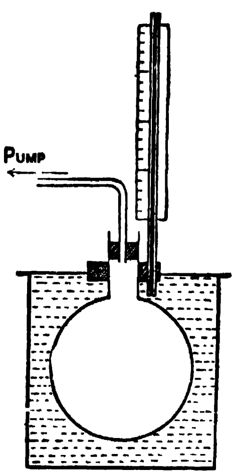


FIG. 3.—Travers' Apparatus (diagrammatic).

Travers devised a method of determining this contraction when the globe was evacuated. The globe was placed inside a closed vessel, with its neck passing through a hole in the stopper (Fig. 3). Also, through another hole in the stopper, passed a calibrated vertical capillary tube. The vessel was completely filled with water, and placed in a thermostat. The globe was then evacuated, and as its volume decreased, the level of the water in the capillary tube fell. From the scale, the volume change could be read off directly.

The actual volume of the globe is determined by filling it with water and weighing. This weight must be corrected for the temperature of the water, and for the weight of air displaced by the globe.

Knowing the weight and the volume of the gas, the density, in grams per litre, can be calculated. For the purpose of molecular weight determination, the density referred to oxygen as 16 is required, and consequently the density of oxygen in grams per litre must be known, or determined. The molecular weight is then calculated as above. Correction must be made for the failure of Avogadro's Hypothesis, and the method of applying this is given on p. 208, § 82.

(*b*) *The Volumeter Method* (Guye and Pintza).—The principle of

the method is the reverse of the last, the volume of a known weight of gas being determined.

The apparatus used by Guye and Pintza in their determination of the density of nitrogen is shown in Fig. 4.

The volumes of the globes A and B were determined by finding the weight of water filling them at 0° C. The volume of the "dead space" between the marks *a* and *b* and the tap G, and the zero of the manometer D were also determined, and the space between the taps E, F and G. The tube H contained coconut charcoal, and was first evacuated and weighed and then attached to the apparatus by a ground-joint (not shown in Fig. 4). The apparatus which was perfectly dry, and had been filled with the gas several times,

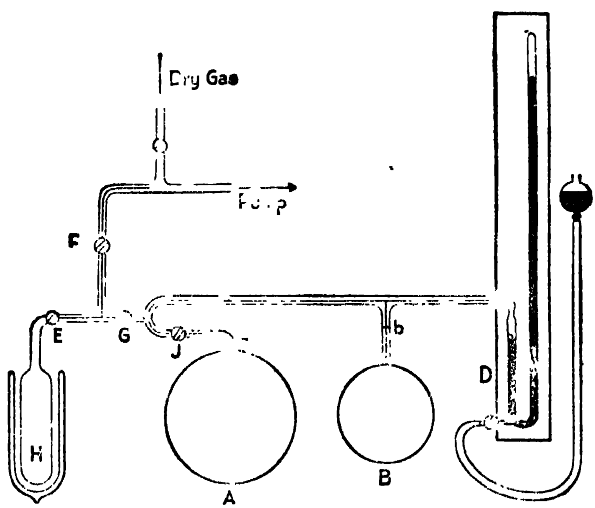


FIG. 4.—Guye and Pintza's Volumeter Method.

was evacuated, and then filled with the gas slowly, up to about atmospheric pressure. The bulbs were immersed in melting ice, and the taps F and G closed, the mercury adjusted to the zero D, and the pressure of the gas read. The space E, F, G, was then evacuated, F closed, and by opening the taps E, G and J, the gas was absorbed by the charcoal in the absorption tube H, the charcoal being cooled in a mixture of solid carbon dioxide and ether. When nearly all the gas had been absorbed, taps E and G were closed, and the pressure of the gas remaining in the apparatus determined. The gas contained in the space EFG was pumped out and measured, and the absorption tube removed from the

apparatus and reweighed. The weight of the gas absorbed by the charcoal was thus found.

From the difference in pressure before and after the experiment, and the amount of gas left in the "dead space," the volume of gas absorbed was calculated. Its weight was known, and hence the density was calculated, corrections being applied for deviations from Boyle's Law.

(c) *The Buoyancy Method.*—A more modern and precise method of measuring gas densities depends upon determining the buoyancy of the gas, and employs a micro-balance. The latter consists of a small quartz bulb, Q (Fig. 5), of about 0·5 c.c. capacity, which is evacuated, and attached to a quartz beam (resting on a knife-edge, K), the motion of which is restricted by two plates, AA. The whole is enclosed in a glass case, provided with an entrance tube, fitted with a tap. The apparatus is so adjusted that after evacuation, and filling with the gas under test at a known pressure, the end of the beam, B, is at the zero position of a scale in a telescope through

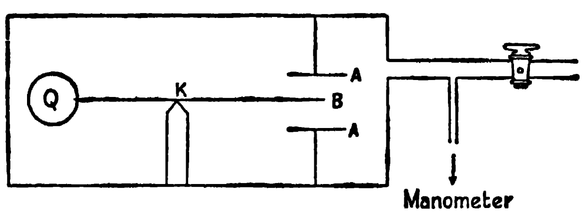


FIG. 5.—Microbalance (very diagrammatic).

which the beam is viewed. The vessel is again exhausted, and oxygen is then admitted to such a pressure that the beam is again at the zero position. Low pressures are used, so that Boyle's Law may be supposed to hold with accuracy for the two gases. It may readily be shown that if D is the density of the gas, D_1 the density of oxygen, p the pressure of the gas, and p_1 the pressure of oxygen,

$$\frac{D}{D_1} = \frac{p_1}{p},$$

or,

$$D = \frac{p_1 D_1}{p}$$

The advantages of the method are that it requires only a very small quantity of gas, and the work is quickly carried out. With a micro-balance similar to that described, the density of radium emanation, of which only 0·75 cubic millimetres was available, was determined. Aston used this apparatus in 1914 to determine

the densities of samples of neon, in attempting to separate its isotopes.

Under certain circumstances, the methods described in § 12 for finding the vapour densities of compounds may be applied to elements.

The buoyancy method has been used by Woodhead and Whytlaw-Gray in the determination of the atomic weights of xenon (1931) and carbon (1933).[1] The balance used in the latter determination was constructed entirely of fused quartz, and was a modification of that previously described, being of the fibre suspension type. The buoyancy bulb in Fig. 6, had a capacity of 8 c.c., and was counterpoised by a smaller bulb with a hole in it, and a small sphere of silica. The method employed was to determine the ratio of the pressures at which carbon monoxide and oxygen have the same

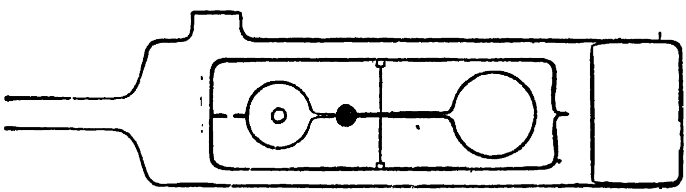


FIG. 6.—Fibre Suspension Buoyancy Balance (Plan).

densities. The balance case was exhausted, and one of the pure gases run in very slowly, through a U-tube cooled in liquid air, until the balance floated. Then a final adjustment of pressure was made until the balance pointer was at the zero mark. The same was repeated with the other gas. Numerous corrections were necessary, which cannot be described here.

The following table gives some of the results :—

TABLE II.—DENSITY OF CARBON MONOXIDE

Series.	Approx. pressures (mm.).		Uncorrected ratio.	Corrections.	Corrected ratio.
	O_2.	CO.			
I. (0° C.)	382·8	437·2	0·87526	−0·00010	0·87516
II. (19·8° C.)	181·9	207·8	0·87535	−0·000123	0·87523
III. (19·8° C.)	361·9	413·5	0·87524	−0·000112	0·87514
IV. (19·8° C.)	572·3	654·0	0·87509	−0·000099	0·87500

[1] *Proc. Roy. Soc.*, 1931, *A*, **134**, 7; *J.C.S.*, 1933, 846.

To obtain the molecular weight of carbon monoxide the value of the ratio at zero pressure (§ 82) must be obtained. This is done by plotting the ratio against the pressure, and continuing the straight line to cut the axis at zero pressure. In this way, three values for the ratio at zero pressure can be obtained from series II., III. and IV. The value from series I. was not considered to be so accurate as those from the other series.

TABLE III.—MOLECULAR WEIGHT OF CARBON MONOXIDE

	Limiting ratios.	Mol. Wt. of Carbon Monoxide.
From Series II. and III.	0·87533	28·010
,, ,, II. and IV.	0·87534	28·011
,, ,, III. and IV.	0·87537	28·011

The molecular weight of the carbon monoxide was calculated from the ratio by multiplying by the molecular weight of oxygen (32). Taking the value for the molecular weight 28·011, this gives 12·011 for the atomic weight of carbon.

It is interesting to note that in connection with the artificial production of elements higher in the periodic table than uranium (the so-called trans-uranium elements, § 42) it has been necessary to devise a balance which will enable quantities as small as 10^{-6} gm.

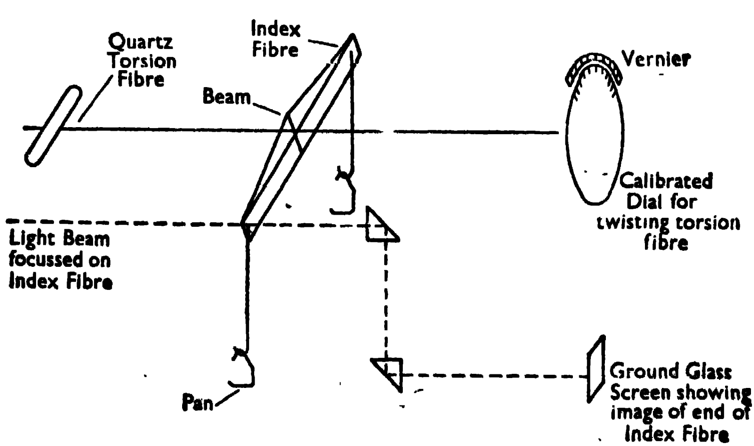


FIG. 7.

to be weighed. The principle used in one type of microbalance (the Salvioni balance) is to measure by means of a microscope the bending of a very fine quartz fibre (approximately 4×10^{-3} cm. in diameter) when it is loaded with the substance to be weighed. In another type of instrument the principle of the torsion balance is used. The twist produced in a fine quartz fibre by the weight to be determined is measured by applying an opposite torsion, which just brings the fibre back to its initial position. An optical method is used to indicate when the exact amount of torsion has been applied. These balances have a sensitivity of 0·02 micrograms. The torsion type has a weighing range of 300 micrograms, and a load capacity of 25 mg.

2. Liquid Elements.—There are only two liquid elements (mercury and bromine), and the atomic weights of these are best determined by converting them into vapours and treating them as gases, or else by using some of the methods for solids.

3. Solid Elements.—The relationship used here is *equivalent* $\times$ *valency* = *atomic weight* (§ 6). It is necessary to determine two things: first the equivalent, and secondly the valency. Since the valency is always an integer, it is clear that the accuracy of an atomic weight determination based on this expression depends upon the degree of accuracy with which the equivalent is determined. As this determination can be carried out with all the accuracy of quantitative chemistry, errors in atomic weights arising from this cause are small.

The more difficult task is to decide the valency of the element. There are several ways of doing this.

(*a*) *The Vapour Density Method.*—In this method the molecular weight of a compound of the element is determined. This can be carried out most conveniently by Victor Meyer's method of determining vapour density (§ 12). For this purpose a compound must be chosen which will vaporise at as low a temperature as possible, and also is not decomposed on vaporisation. As a rule the chloride is the most suitable compound.

Suppose the element A has a valency n. The formula of its chloride will be ACl_n, and, if a is the atomic weight of the element, the molecular weight, M, of the chloride will be $a + 35{\cdot}5\,n$ (since the atomic weight of chlorine is 35·5, approximately). If e is the equivalent, $a = e \times n$. Hence

$$en + 35{\cdot}5\,n = M$$

or

$$n(35{\cdot}5 + e) = M.$$

e and M are known, so n can be calculated. Of course, vapour density determinations will give only an approximate value for M,

so the nearest whole number to the value obtained is taken as the valency. The atomic weight is then obtained by multiplying the accurately determined equivalent by the valency.

(*b*) *The Specific Heat Method.*—As a result of their researches on the specific heats of a number of metals in 1819, Dulong and Petit were able to make the generalisation that the atomic weight of a metal multiplied by its specific heat is equal to 6·4. The Law only holds for metals, and even then there are several exceptions (see § 131). It certainly would not be accurate enough to enable a trustworthy figure for the atomic weight to be found without further and more accurate evidence. Its chief use is to determine the valency of an element, of which the equivalent has been determined with all possible accuracy. The Law is more fully discussed in § 131.

As an example, suppose that the equivalent of a metal has been determined by combining it with chlorine, or precipitation of silver chloride by the chloride of the metal, the following results being obtained: 1·376 gms. of metal combine with 1·000 gm. of chlorine. Owing to the difficult volatility of the chloride, or for other reasons, it is decided to apply the specific heat method rather than find the vapour density of the chloride. The specific heat is found to be 0·032. From the first observations, the accurate equivalent of the metal is $1{\cdot}376 \times 35{\cdot}457 = 48{\cdot}788$. The rough atomic weight is given by the formula, atomic weight $\times$ specific heat $= 6{\cdot}4$. This gives for the rough atomic weight, $6{\cdot}4/0{\cdot}032 = 200$. It is clear that the only value for the valency which will bring the atomic weight anywhere near this figure is 4, and so the *accurate* atomic weight is $4 \times 48{\cdot}788 = 195{\cdot}152$.

(*c*) *Use of the Law of Isomorphism.*—The Law of Isomorphism, which is dealt with more fully in § 146, states that *compounds which have identity of crystalline form* (*i.e.*, isomorphous compounds, which will form mixed crystals) *have similar chemical formulæ.*

Thus the three oxides, ferric, aluminium and chromium (Cr_2O_3), are isomorphous; they occur in the same crystalline form, and can sometimes replace each other in minerals. The formula of aluminium chloride is easily found from the vapour density, since this substance is readily volatile, and Victor Meyer's method can be applied. The formula obtained is $AlCl_3$, when determined at high temperatures, and the formula of the oxide must be Al_2O_3. Since the other oxides are isomorphous with alumina, their formulæ must be Fe_2O_3 and Cr_2O_3, and from the percentage compositions of these oxides as determined by analysis, the atomic weights of iron and chromium can be found.

Isomorphism has proved most useful in correcting atomic weights.

Thus, before 1836, *silver* was supposed to have the atomic weight 216, whilst that of copper was taken to be 63·5. Dumas, in studying the sulphide minerals of copper and silver, found that the minerals chalcocite, Cu_2S, and acanthite, silver sulphide, then written AgS, were isomorphous. For various reasons the figure 63·5 was regarded as correct for copper, and hence the formula of silver sulphide was Ag_2S, and the atomic weight of silver 108.

One of the best examples was the application of isomorphism to the determination of the atomic weight of *vanadium* by Roscoe in 1868. Berzelius assumed in 1831 that the oxide of vanadium was VO_3, and the atomic weight on that basis was 61. This view was held for almost forty years. Rammelsberg in 1856 pointed out that the following minerals were isomorphous :—

Apatite,	$3Ca_3(PO_4)_2 + CaF_2 = Ca_5P_3O_{12}F$.
Pyromorphite,	$3Pb_3(PO_4)_2 + PbCl_2 = Pb_5P_3O_{12}Cl$.
Mimetite,	$3Pb_3(AsO_4)_2 + PbCl_2 = Pb_5As_3O_{12}Cl$.
Vanadinite,	$3Pb_3V_2O_6 + PbCl_2 = Pb_5V_3O_9Cl$.

The formula of the last compound is that based on the Berzelius figure for the valency of vanadium. It is clear that while the first three minerals have analogous formulæ, the last is quite different. Yet all these compounds are isomorphous, and hence their formulæ should be similar, and the valency of vanadium should be 5.

Roscoe showed that Berzelius had actually mistaken an oxide VO for the element itself.[1] The formula which had been written $Pb_5V_3O_9Cl$, should therefore have been $Pb_5(VO)_3O_9Cl$ or $Pb_5V_3O_{12}Cl$. Working with pure compounds he was able to find the atomic weight, 51·4.

Beryllium behaves in many ways like aluminium, and was at first assigned a valency of three, and an atomic weight of 14·1. But Mendeléeff found that it should appear in Group II. in the Periodic Table, and should therefore have a valency of two. The atomic weight would then be 9·4. This alteration was made by Mendeléeff, and was later confirmed by the determination of the specific heat of the element at high temperatures, by the discovery by Mallard that the oxide, beryllia, is isomorphous with zinc oxide, and must therefore have the formula BeO, and by the determination of the vapour density of beryllium chloride.

The atomic weight of *zirconium* was believed to be about 67 for some time. Berzelius first assigned the formula ZrO_3 to the oxide,

[1] It may be thought that if this was so, Berzelius' oxide VO_3 would be really $VO(O_3)$, *i.e.*, VO_4, which disagrees with the valency of 5 mentioned; but in Berzelius' time, oxygen was assigned an atomic weight of 8, and water was written HO; consequently, Berzelius' VO_3 would correspond to V_2O_3 on our system, which would be $(VO)_2O_3$, *i.e.*, V_2O_5, when the Berzelius error was rectified.

Periodic Table

Atomic Numbers thus, 7.

(International Atomic

Valency	I. 1 A.	B.	II. 2 A.	B.	III. 3 A.	B.	IV. 4 A.	B.	V. 3 5 A.	B.
Period 1	Hydrogen, H. 1. *1·0080*									
„ 2	Lithium, Li. 3. *6·940.*		Beryllium, Be. 4. *9·02.*		Boron, B. 5. *10·82.*			Carbon, C. 6. *12·010.*		Nitrogen, N. 7. *14·008.*
„ 3	Sodium, Na. 11. *22·997.*		Magnesium, Mg. 12. *24·32.*		Aluminium, Al. 13. *26·97.*			Silicon, Si. 14. *28·06.*		Phosphorus, P. 15. *30·98.*
„ 4	Potassium, K. 19. *39·096.*	Copper, Cu. 29. *63·57.*	Calcium, Ca. 20. *40·08.*	Zinc, Zn. 30. *65·38.*	Scandium, Sc. 21. *45·10.*	Gallium, Ga. 31. *69·72.*	Titanium, Ti. 22. *47·90.*	Germanium, Ge. 32. *72·60.*	Vanadium, V. 23. *50·95.*	Arsenic, As. 33. *74·91.*
„ 5	Rubidium, Rb. 37. *85·48.*	Silver, Ag. 47. *107·880.*	Strontium, Sr. 38. *87·63.*	Cadmium, Cd. 48. *112·41.*	Yttrium, Y. 39. *88·92.*	Indium, In. 49. *114·76.*	Zirconium, Zr. 40. *91·22.*	Tin, Sn. 50. *118·70.*	Niobium, Nb. 41. *92·91.*	Antimony, Sb. 51. *121·76.*
„ 6	Cæsium, Cs. 55. *132·91.*	Gold, Au. 79. *197·2.*	Barium, Ba. 56. *137·36.*	Mercury, Hg. 80. *200·61.*	Lanthanum, La. 57. *138·92.* Cerium, Ce. 58. *140·13.* Praseodymium, Pr. 59. *140·92.* Neodymium, Nd. 60. *144·27.* Illinium, Il. 61. Samarium, Sm. 62. *150·43.* Europium, Eu. 63. *152·0.* Gadolinium, Gd. 64. *156 9.* Terbium, Tb. 65. *159·2.* Dysprosium, Ds. 66. *162·46* Holmium, Ho. 67. *164·94.* Erbium, Er. 68. *167·2.* Thulium, Tm. 69. *169·4.* Ytterbium, Yb. 70. *173·04.* Lutecium, Lu. 71 *174·99.*	Thallium, Tl. 81. *204·39.*	Hafnium, Hf. 72. *178·6.*	Lead, Pb. 82. *207·21.*	Tantalum, Ta. 73. *180·88.*	Bismuth, Bi. 83. *209·00.*
„ 7	87.		Radium, Ra. 88. *226·05.*		Actinium, Ac. 89.		Thorium, Th. 90. *232·12.*		Protactinium, Pa. 91. 231.	

OF THE ELEMENTS.

Atomic Weights thus, *6·94*.

Weights, 1941, are given.)

VI. 2 6 A.	B.	VII. 1 7 A.	B.	VIII.			
		[Hydrogen, H. 1. *1·0080.*]					Helium, He. 2. *4·003.*
	Oxygen, O. 8. *16·0000.*		Fluorine, F. 9. *19·00*				Neon, Ne. 10. *20·183.*
	Sulphur, S 16. *32·06.*		Chlorine, Cl. 17. *35·457.*				Argon, A. 18. *39·944.*
Chromium, Cr. 24. *52·01.*	Selenium, Se. 34. *78·96.*	Manganese, Mn. 25. *54·93.*	Bromine, Br. 35. *79·916.*	Iron, Fe. 26. *55·85.*	Cobalt, Co. 27. *58·94.*	Nickel, Ni. 28. *58·69.*	Krypton, Kr. 36. *83·7.*
Molybdenum, Mo. 42. *95·95.*	Tellurium, Te. 52. *127·61.*	Masurium, Ma. 43.	Iodine, I. 53. *126·92.*	Ruthenium, Ru. 44. *101·7.*	Rhodium, Rh. 45. *102·91.*	Palladium, Pd. 46. *106·7.*	Xenon, Xe. 54. *131·3.*
Tungsten, W. 74. *183·92.*	Polonium, Po. 84.	Rhenium, Re. 75. *186·31.*	85.	Osmium, Os. 76. *190·2.*	Iridium, Ir. 77. *193·1.*	Platinum, Pt. 78. *195·23.*	Radon, Rn. 86. *222.*
Uranium, U. 92. *238·07.*							

but later altered it to Zr_2O_3. Gmelin, however, gave the oxide the formula ZrO. The vapour density of the chloride was determined by Deville and Troost by Dumas' method, and found to be 8·16 (air = 1). The molecular weight of the chloride must therefore be $8{\cdot}16 \times 28{\cdot}8 = 236$, approximately, since the density of air (O = 16) is 14·4. There must be at least four chlorine atoms in the molecule, since the vapour density is too great for $ZrCl_3$. It is too small for $ZrCl_5$, so the compound was probably $ZrCl_4$. The atomic weight was thus four times the equivalent, 22·3, *i.e.*, 89·2. This was later verified by specific heat observations, and by the fact that the compounds K_2SiF_6, K_2SnF_6, and K_2ZrF_6 were isomorphous. The valency of zirconium must therefore be the same as that of tin and silicon, viz., 4.

The atomic weight of *selenium* was derived from the fact that potassium sulphate, K_2SO_4, and potassium selenate, of which the formula must therefore be K_2SeO_4, were isomorphous. The amount of selenium in a given weight of the selenate was determined, and hence the atomic weight was found.

(*d*) *The Periodic Table.*—The Periodic Table is a method of classifying the elements which has numerous advantages. Many systems of classification of the elements have been proposed, but most have proved unsatisfactory. The Periodic Table is by far the most satisfactory classification.

In 1829, Döbereiner showed that if certain sets of three related elements, which he called triads, were considered, the atomic weight of the central element was the mean of the atomic weights of the extreme elements. Thus, the atomic weight of bromine (according to modern standards) is 79·916; the atomic weights of chlorine and of iodine are 35·457, and 126·92, respectively. The mean of the last two is 81·188, which is not greatly different from the figure for bromine. The Law, which is called the Law of Triads, may also be tested with lithium, sodium, and potassium; calcium, strontium, and barium; sulphur, selenium and tellurium, and others.

Döbereiner noted also another type of triad in which the elements were closely related, but possessed atomic weights very close to each other. Thus, iron, nickel and cobalt, form a related series, but their atomic weights are 55·84, 58·69, and 58·94, respectively.

In 1863, Newlands found that when he arranged the elements in order of ascending atomic weight, commencing with hydrogen, every eighth element commenced a new series, the properties of the elements at the same places in the various series being similar. Thus:—

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

This relationship he called the *Law of Octaves.* It was found, however, that it was not true for the elements of higher atomic weight. It can be seen that even in the three series given above there are certain anomalies, iron, for example, being classified with oxygen and sulphur.

The law found little application, but in 1869 Mendeléeff,[1] quite independently of Newlands, put forward a law which was really an extension of the Law of Octaves. This Law, known as the *Periodic Law,* may be stated as follows :—

The properties of the elements are periodic functions of the atomic weights.

Mendeléeff arranged the elements in series to show this periodic recurrence in properties. Hydrogen had no analogue amongst the other elements, and was therefore placed in a group by itself. Then followed the first and second series, each comprising seven elements (since the discovery of the inert gases, there are now eight elements in these series). Mendeléeff then found it necessary to have a long series, which consisted of two short series joined together by the chain of "transition elements" (*e.g.*, Fe, Ni and Co), making together 18 elements. This was followed by a similar long series, and this again by a series of 32 elements. The remaining series required to finish the table is incomplete. A copy of the Table is given above. This has been drawn up to include all the elements at present known, and therefore differs considerably from that proposed by Mendeléeff.

It is not our purpose to enter into a lengthy discussion of the Periodic Table, as this is part of "Inorganic Chemistry."[2] For our present work, it is sufficient to notice that in the vertical columns are to be found elements that are more or less closely related, and that in any horizontal series the valency with respect to hydrogen increases from 1 to 4 (in Group IV.) and then decreases to 1 again. With respect to oxygen, the valency may increase all the way along the horizontal series from 1 to 7. In these statements, the transition elements in Group VIII. are omitted, and it should be noted that there are some exceptions.

When Mendeléeff constructed the Periodic Table he found it necessary to place some elements in different groups from those into which they would have fallen according to the values of their atomic weights, in order to place them with elements with which their properties were most in accord. Thus, the element *indium* had

[1] In a paper giving an historical survey of the Periodic System, G. Elsen (*Chem. Weekblad*, 1930, **27**, 378) states that a system approximating to that later proposed by Mendeléeff was put forward by one Cooke, as early as 1854.

[2] For a more complete account, the student is advised to see Sherwood Taylor's "Inorganic and Theoretical Chemistry," pp. 147–155.

always been supposed to be bivalent, and to have an atomic weight 75·8. Its bivalency would bring it into Group II. with zinc, but this place is already occupied by strontium, and there is also no room for it between arsenic (75) and selenium (79). The atomic weight was therefore considered to be wrong, and on determination of the specific heat of the element, its atomic weight was found to be 114·5, confirming Mendeléeff's view that it should be placed in Group III.

As stated above, the atomic weight of beryllium was also corrected by this method.

(*e*) *The Physical Method.*—In this method, the relative amounts and respective atomic weights of the different isotopes present in an element are determined. Within recent years it has become possible to determine atomic weights in this way to a degree of accuracy equivalent to that obtainable by ordinary gravimetric analysis. It has the additional advantage that only a very small amount of the element is required for a determination, and the substance used need not be pure. The method is described in detail later (§ 38).

***12. Methods of Determining Vapour Densities.**—In § 11 the determination of vapour density has been referred to as being important in finding atomic weights. It is also a very valuable method of finding the approximate molecular weight of a substance in the gaseous state.

The *vapour density is the ratio of the masses of equal volumes of the vapour and of oxygen, the latter being taken as* 16.

There are several methods of determining vapour density, of which the most frequently used is that due to Victor Meyer. In this, the volume occupied by a known weight of vapour is determined.

The apparatus is shown in the accompanying figure (Fig. 8). A long tube usually made of glass, but sometimes, when higher temperatures are necessary, of porcelain, platinum, or quartz, has a bulb at one end. This tube is the one in which the substance is vaporised. It is surrounded by a jacketing tube made of suitable material. A copper tube, even for comparatively low temperatures, is much more useful than a glass one, although the latter is more commonly used. Glass outer jackets are easily broken, whilst a copper one, though initially more expensive, is almost everlasting. The outer jacket contains some liquid boiling at a considerably higher temperature than the substance to be placed in the inner tube. Where a liquid is used, of which it is not desirable to allow the vapour to escape into the air, a condenser may be fitted. A side tube is attached to the inner tube, bent as shown, and passed under water or mercury in a trough.

A graduated tube is filled with the liquid in the trough, and inverted in it, over the end of the side tube. The substance is introduced into the vaporising tube in a small bottle of the shape shown. As these bottles are expensive and frequently lost, it will be found quite convenient to replace them with home-made small bulb tubes which have no stoppers. First, the inner tube is dried thoroughly, and a little asbestos pad placed at the bottom to break the fall of the bottle when it is put in. A liquid is placed in the outer jacket and heated to boiling until no air bubbles appear in the trough. While this is going on, the small tube is weighed, filled with the substance under investigation, and weighed again. The difference gives the weight of substance taken. The stopper of the vaporising tube is now removed, the graduated tube placed in position over the end of the delivery tube, the small bottle dropped in, and the vaporising tube re-closed. The stopper is immediately blown out by the pressure of the vapour and bubbles of air are collected in the graduated tube. The total volume of air pushed over is the volume of air displaced by the vapour, and is therefore the volume of the vapour. The temperature of the room and the atmospheric pressure are taken, and the volume is also corrected for vapour pressure of water if the air displaced is collected over water. The density of the vapour in grams per c.c. is calculated, and also the density referred to oxygen as 16, from which the molecular weight can be obtained.

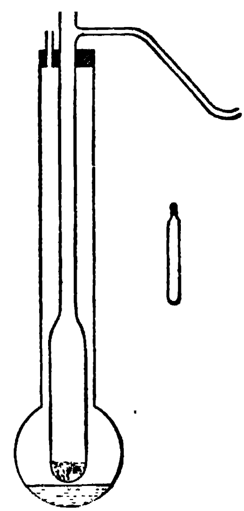


FIG. 8.—Apparatus for Victor Meyer's Method of determining Vapour Densities.

The following is the calculation involved: Let the weight of substance used be W grams, and the volume of vapour, v c.c. Let the temperature of the room be $t°$ C., and atmospheric pressure P mm. If the pressure of water vapour at this temperature is p mm., the actual pressure of the air collected is $P - p$ mm.

The corrected volume of air is V c.c., given by

$$V = \frac{273\,(P - p)\,v}{760\,(t + 273)}.$$

The density of the vapour in grams per c.c. is $\frac{W}{V}$.

The molecular weight of the vapour is $22{,}400 \times \frac{W}{V}$.

A number of modifications of Victor Meyer's apparatus have been proposed, the best of which is that due to Lumsden. Instead of measuring the volume of vapour obtainable from a given weight of liquid under atmospheric pressure, the volume is kept constant and the increase in pressure found. The apparatus is shown in the diagram (Fig. 9). The tube A is a large boiling tube fitted with an outlet at B, through which an air condenser passes. The inner tube C is the vaporising tube, and the heating liquid is placed in A. There is a capillary outlet to the inner tube at D, and two other openings at E and F which are closed when the apparatus is in use. The capillary D is connected to a manometer GH, by means of a

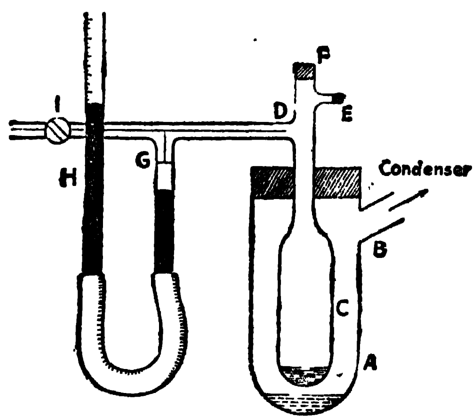


FIG. 9.—Apparatus for Lumsden's Modification of Victor Meyer's Method.

rubber connection which should be wired on. There is a tap at I by means of which the contents of the apparatus may be put at atmospheric pressure. There is a fixed mark on the vertical limb of the manometer G.

For the heating, the boiling tube may be placed on an asbestos box, such as is used for the determination of the elevation of the boiling point (§ 238). A few pieces of glass rod or porous plate are placed in the tube A, together with the heating liquid, and this is boiled. It is also advisable to protect the top of the inner tube from the heat of the burner (this apparatus is considerably smaller than the original Victor Meyer apparatus) by placing a piece of asbestos board over the stopper of the outer tube. During the preliminary heating the tap I is left open to the atmosphere. Enough mercury is poured into the manometer so that when the liquid is at the fixed mark in G, there is a little over the graduated portion in H. The preliminary heating is continued until, when the stopcock I is

closed, the mercury in G remains at the mark. This indicates that constant temperature has been reached. When this is the case, the small bottle (as used in the Victor Meyer apparatus), filled with liquid which has been weighed, is dropped in (asbestos having been placed in the inner tube to break its fall). As the liquid vaporises the pressure increases, and when a steady pressure is attained the tube H is raised to bring the mercury back to the mark on G. It is essential to keep the mercury near the mark by gradually raising H as the pressure increases. The difference in the two levels gives the increase in pressure.

If a liquid of known molecular weight is available, the work is considerably simplified, and the molecular weight of any other easily vaporised liquid can be readily found. The increase of pressure produced by a known weight of the liquid of known molecular weight is found, and the increase which would be produced by 1 gm. molecule is obtained. The pressure produced by a known weight of the liquid under test is determined, and from this the number of grams of it which would produce the same pressure as 1 gm. molecule of the other liquid is calculated. This is the molecular weight.

It need hardly be stated that all vapour must be removed from the apparatus after each determination. The easiest way to do this is to blow a current of air through the apparatus from a foot-bellows.

To find the absolute molecular weight of a substance without making use of an auxiliary substance of known molecular weight, it is necessary to find the volume of the vaporisation tube. This may be done by filling it with water and emptying it out into a measuring cylinder and burette. Then the increase in pressure due to the vaporisation of a known weight of liquid is determined as before.

The calculation is carried out as follows :—

Volume of vaporisation tube . . .	V c.c.
Atmospheric pressure	P mm.

Increase in pressure due to vaporisation of W gms. of liquid = p mm. Consider what would have happened if the substance had been vaporised in an ordinary Victor Meyer apparatus, the pressure being atmospheric, *i.e.* $= P$ mm. The volume of the air and vapour together would have been, say, V' c.c. In this (Lumsden's) apparatus, however, the pressure is increased to $P + p$ mm., and the volume is thereby reduced to V c.c. Hence, by Boyle's Law,

$$PV' = (P + p)\,V.$$

But, the volume of air filling the apparatus at atmospheric pressure $= V$ c.c. Hence, volume of vapour at atmospheric pressure $= V' - V$ c.c., and

$$V' - V = pV/P,$$

i.e., the increase in volume due to the vapour would be equal to the increase in pressure multiplied by the volume of the vaporisation tube and divided by atmospheric pressure. The weight of the vapour is known; the above volume can readily be corrected to N.T.P., and hence the vapour density and molecular weight can be found.

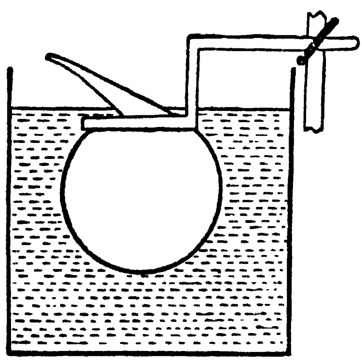


FIG. 10.—Dumas' Apparatus for determining Vapour Density.

2. Another method, devised by Dumas, consists in finding the weight of a known volume of vapour.

A large bulb of the shape shown in Fig. 10 is taken, and weighed full of air. It is then slightly warmed with its mouth under a little of the liquid in a dish. On cooling a few c.c. of the liquid will be sucked into the apparatus. The bulb is then placed in a heating bath, and is conveniently held down by an iron ring, as shown in Fig. 10. The liquid in the heating bath is boiled, and when the last drop of liquid in the bulb disappears, the bulb is sealed off, care being taken to preserve any glass which may have been removed from the end. It is possible to seal the bulb without removing any glass. The bulb is now filled with the vapour of the liquid, and is reweighed, when cool. To find the volume of the bulb, the end is broken off under water, when the water rushes in, as the vapour will now be under considerably reduced pressure. On reweighing the bulb the weight of water which it contains can readily be found, and hence its volume. The temperature and pressure have to be taken (i.) when the bulb is full of air, and (ii.) when the bulb is filled with vapour and is about to be sealed off.

Calculation.

Weight of bulb full of air	$= W$ gms.
Weight of bulb full of vapour	$= w$ gms.
Weight of bulb full of water	$= W_1$ gms.
Temperature at commencement	$= t^\circ$ C.

Pressure at commencement	$= p$ mm.
Temperature just before sealing off	$= T^\circ$ C.
Pressure just before sealing off	$= P$ mm.
Volume of air filling bulb at t° C. and p mm.	$= W_1 - W$ cc.

$$\text{Corrected volume} = \frac{273\, p(W_1 - W)}{760\,(t + 273)}\ \text{c.c.} = V\ \text{c.c.}$$

The weight of this volume of air $=$ $0{\cdot}00129\ V$ gms.

Hence true weight of vapour filling bulb $= w - W + 0{\cdot}00129\ V$ gms. But this filled the bulb at T° C. and P mm., and the volume of the vapour corrected to N.T.P. will be

$$\frac{273\, P(W_1 - W)}{760\,(T + 273)}\ \text{c.c.} = V_1\ \text{c.c.}$$

Hence density of the vapour at N.T.P. $= (w - W + 0{\cdot}00129\ V)/V_1$ gms./c.c. The error should not exceed 2 per cent.

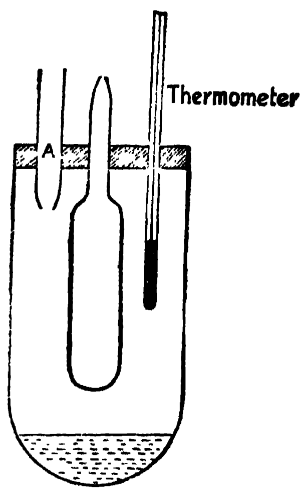


FIG. 11.—Modified Form of Dumas' Apparatus.

A more modern form of the apparatus is shown in Fig. 11. This works on essentially the same principle, and the results are calculated in the same way. The wide outer vessel contains a liquid of higher boiling point than that of which the vapour density is required. The vapour of this liquid heats the bulb, and is condensed by a condenser attached at A. The temperature is read by a thermometer passing through the lid of the vessel. This is a convenient form for carrying out determinations at the higher temperatures.

Another method which is sometimes used is that due to Hofmann. The principle of the method is to introduce a known weight of the liquid into the vacuum at the top of a barometer surrounded by a heating jacket. The liquid evaporates and its volume is measured by the depression of the mercury.

The arrangement of the apparatus is shown in the accompanying diagram (Fig. 12). A small tube (that used for the Victor Meyer determination may be used here) is weighed empty, and then filled with liquid. It is sometimes possible to pour the liquid into these bottles, but if this is not possible, the filling is easily accomplished by warming a little with the mouth of the bottle under some of the liquid in a dish. On cooling, the liquid is

forced in. A piece of glass tube drawn out to a capillary may also be used as a pipette. The bottle is then introduced into the graduated barometer tube, the height of the mercury having been noted. When all the liquid has evaporated, the mercury will reach a constant level, the height of which is again read. The difference between the two gives the pressure to which the vapour is subjected, and the volume of the vapour will be the total volume of the space above the mercury. The temperature will be that of the heating jacket. The corrected volume of vapour is found; its weight is known, and hence the density can be found.

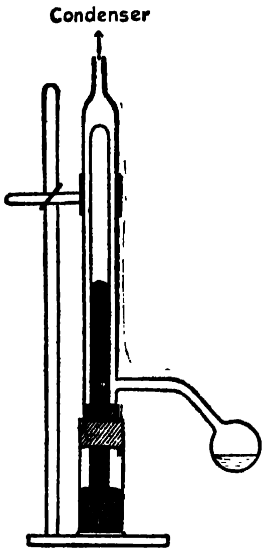


FIG. 12. — Hofmann's Apparatus for determining Vapour Density.

Calculation.

Weight of bottle, empty	$= W$ gms.
Weight of bottle filled with liquid	$= w$ gms.
Hence, weight of liquid taken	$= w - W$ gms.
Volume occupied by vapour	$= V$ c.c.

Pressure $= H - h$ mm., where H is the initial, and h the final height of the mercury in the tube.

Temperature $= T°$ C.

$$\text{Hence, corrected volume of vapour} = \frac{273\,(H - h)\,V}{760\,(T + 273)} \text{ c.c.}$$
$$= V_1 \text{ c.c.}$$

Weight of this volume $= w - W$ gms.

Hence, density $= (w - W)/V_1$ gms./c.c.

The molecular weight of the vapour will be given by $22{,}400 \times D$, where D is the density in gms./c.c.

This method is capable of giving quite accurate results, but the apparatus is cumbersome, and difficult to arrange and read. It also suffers from the disadvantage that, in its ordinary form at any rate, it cannot be used for determining vapour densities at high temperatures.

In another method of determining vapour density, making use of the glass-spring tensimeter, the pressure exerted when a known weight of substance is vaporised at a known temperature is determined. The apparatus is shown in Fig. 13. The vaporisation

bulb, A, is made of glass, or preferably of quartz, and has a flattened spiral tube, B, attached, which is connected to a quartz thread, C. The spiral tube and thread are surrounded by a glass vessel, which can be exhausted, and is supplied with a manometer. The volume of the bulb, A, is determined in a separate experiment, and a known weight of substance is placed in it. The bulb is then exhausted and sealed. On heating in a thermostat or furnace, the substance vaporises, and exerts a pressure which tends to open out the spiral glass spring, and causes a movement of the quartz thread, which can be observed through a telescope, or by means of a mirror, M, attached to the end of the thread. By admitting air to the vessel surrounding the thread and spring, the pressure inside and outside the spring may be made the same, when the pointer will return to its zero position. The pressure of air admitted is measured by means of the manometer, and gives the pressure inside the bulb. The temperature to which the bulb is heated must be determined with accuracy, and this is best done by means of a platinum resistance thermometer, or a thermo-couple. The mass of vapour is known, and also the pressure it exerts when confined in a known space, so that the vapour density is readily calculated.

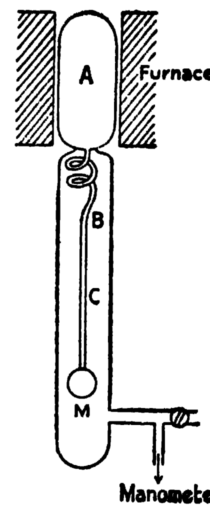


FIG. 13.—Glass-Spring Tensimeter.

13. Some Classical Experiments on combining Weights and Volumes.

1. COMPOSITION OF WATER BY WEIGHT.—(*a*) *Dumas' Method.*—The rather difficult work of finding the ratio in which hydrogen and oxygen combine by weight was first taken up by Dumas in 1842. A diagram of the apparatus is given in Fig. 14.

Hydrogen was made by the action of dilute sulphuric acid on zinc. The gas was impure, and an elaborate system of purification had to be devised. The gas was passed through a series of seven U-tubes containing (1) lead nitrate, to remove hydrogen sulphide; (2) silver sulphate, to remove arsine, stibine, etc.; (3) three tubes containing caustic potash, to remove acid vapours; and (4) a tube of strong sulphuric acid cooled in ice, and a tube containing phosphorus pentoxide to dry the gas.

The purified gas was passed over copper oxide contained in a hard glass bulb tube. This tube was first disconnected from the apparatus, exhausted and weighed. After replacing the bulb tube,

all air was swept out of the apparatus by hydrogen, and the stream of hydrogen continued for ten to twelve hours, during which the copper oxide was heated by means of a spirit lamp. The hydrogen reduced the copper oxide to copper, and water was formed which was collected in a small bulb tube, followed by four drying tubes containing strong sulphuric acid on pumice, or phosphorus pentoxide, the object being to prevent the loss of any water vapour which might not have been condensed in the bulb. The bulb and drying

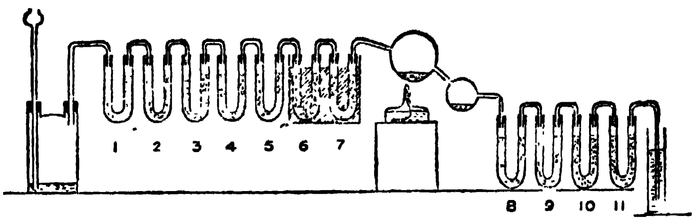


FIG. 14.—Dumas' Apparatus for determining the Composition of Water by Weight.

tubes which had been weighed before the experiment were re-weighed at the end, the difference giving the weight of water produced. The copper produced was allowed to cool in a stream of hydrogen, and the bulb was then disconnected, exhausted and weighed. The difference in weight of this tube before and after the experiment gave the weight of oxygen removed, and which was now in the water. By subtracting this weight of oxygen from the weight of water produced, the weight of hydrogen in the water was obtained.

The result obtained, as a mean of nineteen experiments, was :—

	Per cent. by weight.	Combining ratio.
Hydrogen	11·136	1·00
Oxygen	88·864	7·98

There are several sources of error in this experiment :—

(1) A small quantity of air, dissolved in the sulphuric acid used, passed on with the hydrogen, and the oxygen present consequently combined with some of the hydrogen in the hot copper oxide tube,

(2) The copper, on cooling in hydrogen, absorbed some of the gas.

(3) The drying of the gas with strong sulphuric acid produced some sulphur dioxide, which on passing over the heated copper oxide with hydrogen lost its oxygen, water being formed. The sulphur remaining combined with the copper to form cuprous sulphide.

$$SO_2 + 2H_2 = 2H_2O + S,$$
$$2Cu + S = Cu_2S.$$

Various improvements have been made in this method. Keiser used hydrogen adsorbed in palladium. The gas was pumped over heated copper oxide, the water formed being weighed. The weight of hydrogen used was obtained by weighing the palladium before and after the experiment, and thus it was not necessary to weigh the copper oxide.

(*b*) *Morley's Method.*—The classical experiment of Morley for the determination of the composition of water by weight is now taken as providing the most accurate ratio. Indeed, it has been said that this is the most accurate chemical research ever carried out.

The gases, hydrogen and oxygen, were very carefully purified and weighed in glass globes. A tube was constructed of the form shown in Fig. 15, which has two drying tubes, *aa*, and two platinum jets, *pp*. The tube was exhausted and weighed. The gases were then passed into the apparatus, one down one side, and one down the other, and they were ignited at the platinum jets by passing sparks between the electrodes, *ee*. During the combustion, the tube was immersed in cold water, and at the end of the experiment it was placed in a freezing mixture to freeze the water produced. The excess gas was then pumped out of the apparatus, being dried on its way by the drying tubes, *aa*, and was analysed. The total weight of hydrogen and oxygen used was found to agree with the weight of water formed.

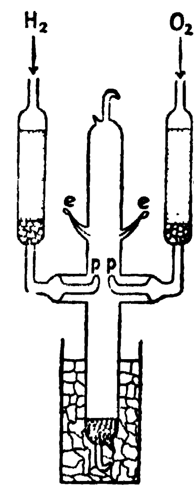


FIG. 15.—Morley's Combustion Tube.

The mean result of twelve experiments was :—

$$\text{hydrogen : oxygen} = 1 : 7{\cdot}9396$$
$$= 1{\cdot}0076 : 8{\cdot}0000$$

(*c*) *Noyes' Method.*—This method, which also gives very accurate results, was developed by Noyes in 1908. The apparatus is shown

in Fig. 16. Pure hydrogen was prepared by the electrolysis of barium hydroxide solution in an apparatus somewhat similar to that used by Burt and Edgar some time later in determining the volumetric composition of water (Fig. 17). The gas was passed into a tube containing palladium, the tube having previously been exhausted. Pure oxygen, also made by the electrolysis of baryta, was now pumped in, whilst the tube containing the palladium-

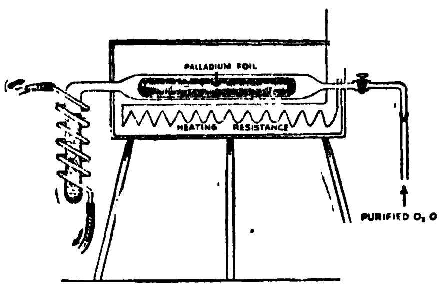


FIG. 16.—Noyes' Apparatus.

hydrogen was heated. Combination of the hydrogen and oxygen took place, with the formation of water, which was collected in a cooled tube, weighed before and after the reaction. The gases left in the tube were pumped off and weighed. The weight of hydrogen in the water was given directly by the difference in weight of the palladium before and after the experiment, whilst the weight of oxygen was obtained by finding the weight of water, and subtracting the weight of hydrogen from it. As a mean of several experiments, the ratio of the weights of hydrogen to oxygen in water was found to be 1·0078 : 8.

2. THE COMPOSITION OF WATER BY VOLUME.—This was a somewhat easier problem than the determination of the gravimetric composition, and consequently we find that it was determined much earlier than the latter. In 1781, Cavendish made a determination using the explosion method, and obtained, as a result, the ratio hydrogen : oxygen = 202 : 100. In 1801, Nicholson and Carlisle discovered that water could be decomposed by passing an electric current through it, and Cruickshank collected the gases and found the ratio of their volumes.

Gay-Lussac and Humboldt, in the course of their experiments on the combining volumes of gases which ultimately led to the Law of Gaseous Volumes, found the ratio hydrogen : oxygen to be 199·89 : 100, and Bunsen found 200 : 100.

The most accurate of the experiments made on the determination of this combining ratio during the last century were those of

Alexander Scott, between 1887 and 1893. The hydrogen was obtained by passing steam over sodium, and the oxygen by heating silver oxide. The purified gases were exploded, and the ratio found was hydrogen : oxygen = 200·285 : 100.

By converting the weights in Morley's experiment to volumes by means of the known densities of the gases, the ratio obtained was 200·269 : 100.

The most accurate research carried out for the determination of the volumetric composition of water was that of Burt and Edgar (1915). The gases were obtained in a specially pure state by the electrolysis of barium hydroxide solution in the apparatus shown in Fig. 17.

The hydrogen was dried by passing over caustic potash and

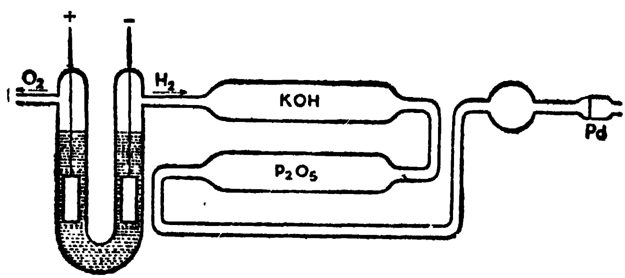


FIG. 17.—Burt and Edgar's Apparatus for the Preparation of Pure Hydrogen.

phosphorus pentoxide, and then further purified by one of two methods : either by passing the gas over coconut charcoal cooled in liquid air, which absorbs oxygen and nitrogen, but hydrogen hardly at all, or by passing through a tube containing palladium black, which causes the combination of any oxygen present with hydrogen, to form water catalytically. The gas was then passed through a palladium membrane heated electrically. This is permeable to hydrogen, but not to any other gas.

The oxygen was prepared in the same apparatus, being passed out from the anode side of the U-tube, liquefied and fractionated. Another method was sometimes used to obtain the oxygen, viz., the action of heat on pure potassium permanganate, washing the gas with strong caustic potash solution, baryta solution, and again with potash. It was then dried, liquefied and fractionated.

The gases, obtained in this way in a state of high purity, were passed into a special explosion apparatus, for details of which the original paper must be consulted. The special advantage of the apparatus was the fact that the actual determinations were carried out at 0° C., and under a pressure of 1 atmosphere, thus avoiding

temperature and pressure corrections. As a mean of fifty-nine experiments, the ratio found was hydrogen : oxygen = 2·00288 : 1 at N.T.P.

This is regarded as the most accurate value yet obtained for the volumetric composition of water.

It is interesting to note that the variations in the results obtained by these methods may be explained, at least partially, by the existence of a heavy isotope, H^2, and of heavy water. Some doubt is thrown upon the accuracy of all the experiments described owing to a lack of knowledge of how far the heavy isotope was separated from the hydrogen used.

In ordinary hydrogen, the ratio of the masses of the light H_2^1, to the heavy H_2^2, is given by Rutherford as 6,500/1. Thus 6,501 mg. of the mixture will react with the same weight of oxygen as 6,500 mg. of the H_2^1 gas, which makes a difference of nearly 0·0002 in the equivalent. The results of Morley and Noyes are 1·0076 and 1·0078 respectively, showing a degree of uncertainty not far from the 0·0002 mentioned. Presumably the preparation of hydrogen by electrolysis, or by the action of acid on zinc, lowers the proportion of H_2^2 or H^1H^2 in the gas, for heavy water is obtained from the residues of electrolysis experiments. The effect of adsorption in palladium on the relative proportions of the isotopes, is at present unknown.

Summary

The Laws of Chemical Combination comprise :—

1. *The Law of Conservation of Matter* (Lavoisier, 1774).—"The total amount of matter in the universe is unaltered, whatever changes take place in its distribution."

The Law was verified by Landolt. It is not strictly true owing to loss of mass in radiation.

2. *The Law of Constant Proportions* (Proust, 1799).—"When combination takes place between elements, it is in definite proportions by weight, so that the composition of a pure chemical compound is independent of the method by which it is prepared."

The converse of this Law is not true, owing to the existence of isomerides.

3. *The Law of Multiple Proportions* (Dalton, 1803).—"When two elements, A and B, combine to form more than one compound, the weights of A which combine with a fixed weight of B are in the proportion of small whole numbers."

4. *The Law of Reciprocal Proportions* (Richter, 1792–94).—"The weights of two or more substances which separately react chemically with identical weights of a third are also the weights which react with each other, or simple multiples of them."

From this follows the *Law of Equivalents*, which states that "substances combine together in the ratio of their equivalents."

The *equivalent* of an element or compound is defined as the weight of it which will combine with, or displace, 8 parts by weight of oxygen.

The standard used in the determination of equivalents and atomic weights is the oxygen standard. Its advantages over the older hydrogen standard are (1) as it is easier to make compounds with oxygen than with hydrogen, atomic weights were usually determined through oxygen. Any error in the atomic weight of this element meant recalculation of many others ; and (2) the hydrogen atom is very light, and experimental errors are therefore magnified.

The chief methods for determining equivalents are :—

(1) Determination of the volume of hydrogen liberated by a known weight of the element from an acid or alkali.
(2) Determination of the weight of the substance that will combine with 8 gms. of oxygen.
(3) Determination of the weight of silver necessary to precipitate a known weight of the chloride of the element.
(4) By displacement of another element of known equivalent from combination.
(5) By conversion into another compound.
(6) By volumetric methods.

5. *The Law of Combining Volumes* (Gay-Lussac, 1808).—"When gases combine, they do so in volumes which bear a simple relationship to each other, and to the product if that is also gaseous."

The atomic theory of Dalton assumed that :—

(*a*) Elements are made up of atoms, which are indestructible. All atoms of the same element have the same weight, and are similar in size and shape.
(*b*) Compound atoms are formed by the union of elementary atoms in simple proportions.

Consideration of the Law of Combining Volumes led *Avogadro* to put forward his *Hypothesis*, which states that "equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules."

The chief *methods of determining atomic weights* are :—

1. *Gaseous Elements*.—Determination of density, and use of the relationship, vapour density = molecular weight/2, after correction for deviations from the Gas Laws.

Gas densities are determined by :—

(*a*) *Regnault's method* of direct weighing of a known volume of the gas.

(*b*) *Guye and Pintza's Volumeter method* of finding the volume of a known weight of gas.

(*c*) The *buoyancy method*, using a micro-balance.

2. *Liquid Elements*.—Conversion into vapour, and proceeding as in 1; use of methods for solid elements.

3. *Solid Elements*.—Determination of equivalent, and use of the relationship, equivalent × valency = atomic weight. Valency can be found :—

(*a*) By finding the vapour density and molecular weight of a volatile compound.

(*b*) By the specific heat method. Specific heat × atomic weight = 6·4 (approx.).

Other methods include the use of the Law of Isomorphism, which states that compounds which have identity of crystalline form have similar chemical formulæ. This has been used in finding the atomic weights of silver, vanadium, beryllium, zirconium, selenium. The Periodic Table has also been useful in the correction of atomic weights, particularly those of indium and beryllium.

The physical method of determining the isotopic composition of an element is now finding considerable application.

The *vapour density* of a substance may be determined by the following methods :—

(*a*) Victor Meyer's method of finding the volume of a known mass of vapour.

(*b*) Dumas' method of finding the mass of a known volume of vapour.

(*c*) Hofmann's method, using a barometer tube.

(*d*) Use of the glass-spring tensimeter.

Some Classical Experiments on Determination of Combining Weights and Volumes.—The composition of water by weight was determined by *Dumas* by oxidising the hydrogen by means of copper oxide, and weighing the copper and water produced.

Morley burnt oxygen and hydrogen and weighed the water produced. A similar method was used by *Noyes*.

The composition of water by volume was determined by Cavendish, Gay-Lussac, Alexander Scott, and Burt and Edgar. The results were :—

Composition by weight	H : O	Composition by volume	H : O
Dumas	1·002 : 8·00	Cavendish	2·02 : 1
Morley	1·0076 : 8·00	Gay-Lussac	1·9989 : 1
Noyes	1·0078 : 8·00	Scott	2·00285 : 1
		Burt and Edgar	2·00288 : 1

It is not to be expected that the results will agree closer than this, owing to the existence of the hydrogen isotope.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 1.—Determine the equivalents of

(*a*) Zinc by replacement of hydrogen in an acid (p. 9).

(*b*) Copper by the displacement method (p. 11).

(*c*) Tin by action of nitric acid and formation of stannic oxide (p. 9).

(*d*) Sodium by the silver chloride method (p. 10).

Experiment 2.—Determine the density of carbon dioxide.

A round-bottomed flask is provided with a well-fitting rubber stopper, through which passes a piece of glass tubing closed with a piece of rubber tubing bearing a clip (Fig. 18). Weigh the flask full of air, noting temperature and pressure. Now fill the flask with dry carbon dioxide, close it, and weigh again. Now open the clip with the tubing under a strong solution of caustic soda (1 in 3). The solution enters the flask, occupying the volume previously taken up by the gas. There will be a residual bubble of air, which will be under reduced pressure. For accurate results the level of the liquid inside and outside the flask should be the same before closing the clip, but if this is impracticable, the error will be small. Note the volume of the soda solution that entered. For this experiment it is necessary to know the weight of 1 c.c. of air. The results are easily worked out (correct for temperature and pressure). If the weight of 1 c.c. of air is not assumed, the flask must be carefully evacuated and weighed before filling with carbon dioxide.

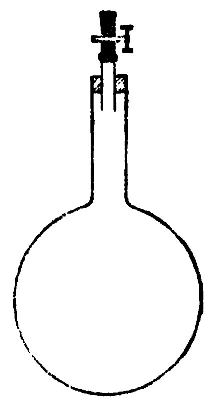


FIG. 18.—Apparatus for Experiment 2.

Experiment 3.—Determine the density of ammonia.

For this experiment standard solutions of sulphuric acid and of sodium hydroxide are required. The flask, which should be of the type used in Experiment 2, must be filled with ammonia (a gas lighter than air). It is then opened under normal sulphuric acid, which enters the flask, and the clip is closed. The volume of acid entering is noted. The weight of ammonia in it is determined by titrating the excess of acid with normal caustic soda.

Experiment 4.—Determine the vapour density of chloroform by Victor Meyer's method. (See § 12.)

Experiment 5.—Determine the vapour density of benzene by Lumsden's method. (See § 12.)

(*a*) *Comparative Method.*—Assuming the molecular weight of ether to be 74, it is possible to find that of benzene very easily with Lumsden's apparatus. Weigh empty a small vapour density bottle; then fill it with ether and weigh again. The difference between these two weights gives the weight of ether taken. Put water into the outer jacket and boil, proceeding as stated above until a constant temperature has been attained. Then introduce the bottle, shut the tap, and determine the increase in pressure. Clean out the apparatus by blowing a current of air through, and then repeat exactly as above for benzene. The calculation of the result has been indicated above (§ 12).

(*b*) *Absolute Method.*—The volume of the vaporising tube is first found, and the increase in pressure due to the vaporisation of a known weight of benzene is found just as before. The result is calculated as indicated above (§ 12).

Experiment 6.—Determine the vapour density of acetone by Dumas' method. (See § 12).

Experiment 7.—Determine the atomic weight of carbon.

The problem resolves itself into two parts : (*a*) the determination of the equivalent of carbon, and (*b*) the determination of the valency of carbon by finding the vapour density of its chloride, *i.e.*, carbon tetrachloride.

(*a*) *Determination of the Equivalent of Carbon.*—It is this part of the work that must be done with as great accuracy as possible.

For this purpose, a known weight of pure carbon is burnt in oxygen and the amount of carbon dioxide formed is weighed. From this it is easy to calculate the equivalent of carbon.

It is first necessary to prepare a pure form of carbon. One of the best for this purpose is sugar charcoal, which is easily made by acting

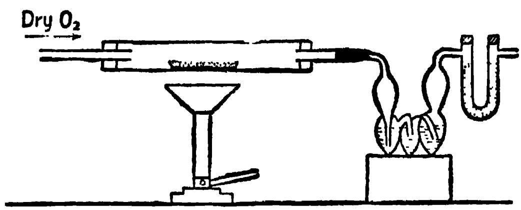


FIG. 19.—Apparatus for determining the Equivalent of Carbon.

on cane sugar with strong sulphuric acid. The sugar chars, losing water and becoming converted into a form of carbon. The mass is mixed with water and boiled in order to dissolve out any unchanged sugar, and is then filtered off. The washing is continued with hot water for some time in order to make quite certain that all unchanged sugar has been removed. The charcoal is then carefully dried in an air oven, heated to 110° C. About ½ gm. of this charcoal is weighed out into a porcelain boat containing some black copper oxide, which is placed in a combustion tube (Fig. 19). The tube is connected at one end with a source of dry oxygen. This may be an aspirator containing oxygen, or, better, a cylinder, the gas being dried by strong sulphuric acid. The other end of the tube is connected to a series of potash bulbs, which are half filled with 30 per cent. potash, and a calcium chloride tube, which are weighed at the beginning of the experiment. The carbon is now heated to redness in the combustion tube, and a slow stream of oxygen is passed over. The stream of gas should be slow enough for the bubbles passing through the bulbs to be counted with ease. When all the carbon has disappeared, the potash bulbs are weighed again. The increase in weight gives the weight of carbon dioxide absorbed. Knowing the weight of carbon from which this originated, it is easy to calculate the equivalent of the element. In order to sweep all the carbon dioxide out of the tube, it is necessary to pass dry air (carbon dioxide free) through the tube for a few minutes after all the carbon has disappeared.

The second step, that of finding the valency of carbon, has now to be undertaken.

(*b*) *Determination of the Vapour Density of Carbon Tetrachloride.*—It is essential to use pure carbon tetrachloride. The method used can be either that of Victor Meyer or that of Lumsden. As the boiling point of carbon tetrachloride is about 77° C., it is necessary to use water, or some heating liquid with a boiling point even higher than that of water, in the outer jacket. The details for this determination are described in § 12.

Having found the vapour density of the chloride, its molecular weight can be found, and, knowing the equivalent, the valency is found as described above (§ 11, 3*a*).

Experiment 8.—Determine the atomic weights of silver, potassium, chlorine, bromine, iodine, sodium and lithium, by methods due to Stas.

Although methods are given for the complete determination of the atomic weights of all the above elements, the experiment need not be carried to completion if there is insufficient time. The experiment is easily stopped at any stage.

It is assumed that the atomic weight of oxygen is 16. The method involves the determination of the following ratios :—

$$\begin{aligned} \mathrm{KCl} &: \mathrm{O} \\ \mathrm{KCl} &: \mathrm{Ag} \\ \mathrm{AgCl} &: \mathrm{Ag} \\ \mathrm{AgBr} &: \mathrm{Ag} \\ \mathrm{AgI} &: \mathrm{Ag} \\ \mathrm{NaCl} &: \mathrm{Ag} \\ \mathrm{LiCl} &: \mathrm{Ag}. \end{aligned}$$

(*a*) *Determination of the Formula Weight of KCl.*—Weigh out into a crucible of known weight about 1 gm. of potassium chlorate, and heat, at first gently, then more strongly over a Bunsen until all oxygen is evolved. Allow to cool and weigh. Then reheat for five minutes and weigh again. Repeat this process until a constant weight is reached. The weight of KCl which combines with 48 gms. of oxygen is then calculated, and is the formula weight required. Great care must be taken to avoid loss of chlorate.

(*b*) *Determination of the Ratio KCl : Ag.*—Weigh out about 2·5 gms. of silver foil, and dissolve it in slight excess of dilute nitric acid. Make the solution up to 500 c.c. This solution will serve for a number of the further determinations. Make a standard solution of KCl of such strength that the potassium chloride and silver nitrate solutions are roughly equivalent. Take 25 c.c. of the silver solution, and titrate it with the standard KCl without the use of an indicator (remember that the $AgNO_3$ is still somewhat acid). In this way calculate the amount of KCl combining with a given weight of silver, and hence obtain the ratio

$$\mathrm{KCl} : \mathrm{Ag}.$$

Since we know the formula weight of KCl (O = 16) we have the atomic weight of silver.

(*c*) *Determination of the Ratio Ag : AgCl.*—Take 100 c.c. of the silver solution and add to it a slight excess of dil. HCl. Boil for a short time, decant off the liquid from the ppt. of silver chloride, and wash the precipitate by decantation. Filter off through a Gooch crucible, the weight of which is known. Take care to keep the precipitate from the light. Wash thoroughly and dry the Gooch and precipitate in an oven,

and weigh again. The difference is the weight of silver chloride. Knowing the weight of silver in the original solution, we obtain the ratio Ag : AgCl, and knowing the atomic weight of silver we can get the formula weight of silver chloride, and hence the atomic weight of chlorine.

(*d*) *Determination of the Ratio Ag : AgBr, and Ag : AgI.*—In each case take 100 c.c. of the silver solution and add a slight excess of potassium bromide and potassium iodide respectively. Filter off the precipitates of silver bromide and silver iodide, proceeding exactly as above. In this way we obtain the ratios Ag : AgBr and Ag : AgI, and knowing the atomic weight of silver the formula weights of the bromide and iodide can be found, and hence the atomic weights of the elements.

(*e*) *Determination of the Ratios NaCl : Ag, and LiCl : Ag.*—Instructions are given for the ratio NaCl : Ag. The other determination is exactly the same except that lithium is to be substituted for sodium.

Take about ½ gm. of pure sodium chloride (accurately weighed) and dissolve it in 100 c.c. of water. Then titrate this solution against the silver solution already prepared. As this is slightly acid it is necessary to titrate without an indicator. The result of this titration will give the amount of sodium chloride corresponding to a given weight of silver, and hence the ratio NaCl : Ag can readily be found. Knowing the atomic weight of chlorine, the atomic weight of sodium is found by subtraction. In this way the atomic weights of almost any elements can be found. We have given here examples of the determination of seven atomic weights by simple quantitative analysis. It will be noted that they all depend on the atomic weights of silver and chlorine, and hence a slight error in the determination of one of these will cause an error all the way through.

Summary of Results.

KCl : O	= 4·659 : 1·000	*Formula weight of KCl*	= 74·557.
KCl : Ag	= 0·690 : 1·000.	*Atomic weight of Ag*	= 107·88.
AgCl : Ag	= 1·327 : 1·000.	*Atomic weight of Cl*	= 35·457.
AgBr : Ag	= 1·740 : 1·000.	*Atomic weight of K*	= 39·10.
AgI : Ag	= 2·176 : 1·000.	*Atomic weight of Br*	= 79·916.
NaCl : Ag	= 0·542 : 1·000.	*Atomic weight of I*	= 126·92.
LiCl : Ag	= 0·392 : 1·000.	*Atomic weight of Na*	= 22·997.
		Atomic weight of Li	= 6·940.

Experiment 9.—Determine the atomic weight of copper, making use of Dulong and Petit's Law.

The method resolves itself into two parts. First, the determination of the specific heat of copper, and secondly, the determination of the equivalent of the metal.

(*a*) *Determination of the Specific Heat of Copper.*—It is not necessary to determine the specific heat with any great accuracy, as the Law of Dulong and Petit is at the best only approximately true. For chemical purposes, it is essential to use glass calorimeters, as often the heats of reaction of substances which would attack metal have to be found. For this purpose, two beakers are chosen which fit one inside the other. A layer of felt is placed between the two, and in this way a fairly good glass calorimeter may be made. A much more satisfactory method, however, is to use small thermos flasks as calorimeters. These are quite cheap, and are extremely useful for thermochemical determinations. First of all the water equivalent of the calorimeter has to be determined.

This may be done by heating a known weight of water to, say, 50° C., and pouring it into a known weight of water in the calorimeter, and noting the highest temperature attained. From these weights and the temperature, the water equivalent of the calorimeter can be calculated, and when once determined is best noted on a label which is attached to the calorimeter. This saves further determination later on. To determine the specific heat of copper, a piece of copper is weighed, and heated to 100° C., by placing it in a test-tube heated for five minutes in boiling water. A piece of thread should be attached to the metal to facilitate its removal from the tube. The temperature of a known weight of water in the calorimeter is taken, and the hot piece of copper is carefully lowered into the water as quickly as possible. The water is stirred, and the highest temperature reached is recorded. There is no need to take into account the cooling correction of the calorimeter, as it is not necessary to get an extremely accurate result. The specific heat of the copper can then be found as shown below.

Calculation of the Water Equivalent of the Calorimeter.—Let the water equivalent be W; let the mass of water in the calorimeter initially be w_1 gms., and its temperature t_1° C. Let the mass of water added be w_2 gms., and its temperature t_2° C. Let the final temperature be t_3° C.

The amount of heat given out by the added water is $w_2\ (t_2 - t_3)$ calories.

The amount of heat taken up by the calorimeter and contents is $(W + w_1)\ (t_3 - t_1)$ calories.

Hence $$(W + w_1)\ (t_3 - t_1) = w_2\ (t_2 - t_3).$$

W is the only unknown in this equation, and is readily calculated.

Calculation of the Specific Heat of the Copper.—Let the weight of the copper be w_3 gms., and the weight of water in the calorimeter w_4 gms. Let the initial temperature of the water be t_4 °C., and the final temperature t_5° C. The copper is cooled from 100° C. to t_5° C., and, if its specific heat is s, the amount of heat given out is $w_3 s\ (100 - t_5)$ calories. The water and the calorimeter are heated from t_4° C. to t_5° C., and the amount of heat thus taken up is $(W + w_4)\ (t_5 - t_4)$ calories. These two amounts are equal. Thus

$$w_3 s\ (100 - t_5) = (W + w_4)\ (t_5 - t_4),$$

and from this equation s can be calculated.

(*b*) *Determination of the Equivalent of Copper.*—This is best done by converting a known weight of metal into the oxide, and then calculating the weight of metal which will combine with 8 gms. of oxygen.

Weigh out accurately about 0·5 gm. of copper turnings, and dissolve in as small a quantity of 1 : 1 nitric acid as possible. During this operation, which should be carried out in a beaker, care should be taken to prevent loss by spirting. Heat the liquid, which should be diluted to about 100 c.c. with distilled water, to boiling, and then add boiling caustic soda solution until present in excess. Boil the liquid and allow the precipitate to subside. The colour of the liquid above the precipitate should not be green. Decant the liquid through a previously prepared and weighed Gooch crucible, wash the precipitate in the beaker twice with boiling distilled water, and then transfer it to the Gooch. Continue to wash till the washings give no precipitate with silver nitrate. Dry the Gooch in the steam oven, place it inside a nickel crucible, and heat to redness. After about fifteen minutes it is allowed

to cool, and is reweighed, the difference in weights giving the weight of copper oxide formed. From this the equivalent of the metal is readily calculated.

SUGGESTIONS FOR FURTHER READING

"Foundations of the Atomic Theory" (Dalton, Wollaston, T. Thomson, 1802–8). *Alembic Club*, No. 2.
"Foundations of the Molecular Theory" (Dalton, Gay-Lussac, Avogadro, 1808–11). *Alembic Club*, No. 4.
"A Course of Chemical Philosophy" (Cannizzaro, 1858). *Alembic Club*, No. 18.
YOUNG, S. "Stoichiometry." (*Longmans, Green*, 1918.)
CAVEN, R. M. "The Foundations of Chemical Theory." (*Blackie*, 1920.)

QUESTIONS

(The atomic weights used throughout this book are those given in the Table on p. 754.)

(1) Describe an experiment which could be carried out in the laboratory to verify the Law of Constant Proportions for one compound.

(2) How would you determine the equivalent of potassium ?

(3) How has the Law of Conservation of Matter been verified ? What are the modern views as to the exactness of this Law ?

(4) In what way does the existence of isotopes affect the Law of Constant Proportions ?

(5) What were the assumptions of Dalton's atomic theory ? How did the term "molecule" arise ?

(6) What refinements would you introduce into the ordinary laboratory method of determining the volumetric composition of sulphur dioxide to make it one of greater accuracy ?

(7) Give an account of the work of Stas on the determination of equivalents and atomic weights.

(8) Describe the various methods available for determining the atomic weight of an element which does not form volatile compounds.

(9) The following facts are known concerning a solid element :—

(*a*) Combined with oxygen it gives a base.

(*b*) Its specific heat is 0·119.

(*c*) 10·00 Gms. of the element will unite with 4·298 gms. of oxygen.

(*d*) 8·00 Gms. of the element will combine with 10·159 gms. of chlorine.

What conclusions can be drawn from each of these data concerning the atomic weight of the element ?

(10) In a recent determination of the atomic weight of iodine, a known weight of silver iodide was converted into silver chloride, which was weighed. In three sets of experiments, the following results were obtained :—

Wt. of AgI.	Wt. of AgCl.
14·41889	8·80228
17·91554	10·93678
10·72744	6·54879

the weights being given in grams. Assuming the atomic weights of silver and of chlorine to be 107·88 and 35·457 respectively, calculate the atomic weight of iodine from these data, correct to three places of decimals.

(11) In the determination of the atomic weight of lanthanum by Baxter and Behrens (*J. Amer. Chem. Soc.*, 1932, **54**, 591), pure lanthanum bromide was added to silver nitrate and the precipitated silver bromide weighed. The following are some typical results :—

Wt. of $LaBr_3$.	Wt. of AgBr.
4·01090	5·96743
5·19186	7·72475
6·57727	9·78548

the weights being given in grams. Assuming the atomic weights of silver and bromine to be 107·88 and 79·916 respectively, calculate the atomic weight of lanthanum.

(12) Roscoe, in determining the molecular weight of vanadium chloride (1878) used Dumas' method, with the following results: weight of globe full of air (9° C., 760 mm.), 24·4722 gms.; weight of sealed globe (9° C., 760 mm.), 25·0102 gms.; temperature of bath when sealing globe, 215° C.; height of barometer when sealing globe, 762 mm.; weight of globe full of water, 194·00 gms. Calculate the molecular weight of vanadium chloride (1 c.c. of air at N.T.P. weighs 0·001293 gms.).

(13) In the determination of the molecular weight of chloroform vapour by Hofmann's method, the following results were obtained; weight of liquid in bulb, 0·2704 gms.; volume of vapour, 110 c.c.; temperature of vapour, 99·6° C.; atmospheric pressure, 747 mm.; height of mercury in the tube. 285·2 mm. Calculate the molecular weight of the chloroform.

(14) Hönigschmid and Sachtleben (*Z. anorg. Chem.*, 1931, **195**, 207) determined the atomic weight of sulphur by synthesising silver sulphide from its elements. Some of the results are given below :—

Wt. of Ag (gms.).	Wt. of Ag_2S (gms.).
7·90291	9·07742
9·74522	11·19355
10·75224	12·35021
9·84439	11·30748

Calculate the value of the ratio $Ag_2S : 2Ag$, and thence the atomic weight of sulphur (Ag = 107·880).

(15) Baxter and Bliss (*J. Amer. Chem. Soc.*, 1930, **52**, 4848) determined the atomic weight of lead from various sources with the following results :—

Sample.	Wt. of $PbCl_2$. gms.	Wt. of Ag. for complete precipitation. gms.
Common	2·74332	2·12809
	3·60741	2·79852
Kolm	1·61294	1·25678
	1·60407	1·24983
Uraninite	3·74779	2·91608
	5·63102	4·38436

Calculate the atomic weight of lead from each source, and explain the results (see § 41).

CHAPTER II

ATOMIC STRUCTURE—PART I

14. The Conduction of Electricity through Liquids.—The discovery of the Voltaic pile in 1800 marked the opening of a new epoch in the history of physics and chemistry. The working of the cell itself was a matter of great interest, and involving as it did the passage of a current through a liquid, research was very soon centred on this aspect of the subject. Indeed, in the year 1801, Nicholson and Carlisle, as mentioned in the previous chapter (§ 13), decomposed water by passing the electric current through it.

The chief investigator in this branch of science at this time was Sir Humphry Davy, who prepared the alkali metals, sodium and potassium, by electrolysis of the moist hydroxides, *i.e.*, strong solutions of the hydroxides. This work was done in the years 1807–8. During this time, Berzelius and Hisinger, in Sweden (1803–7), had been studying the effect of passing the current through solutions of neutral salts, using various electrodes, and noting the products. In this way, during the first decade of the nineteenth century, a large amount of qualitative data was obtained. So far no quantitative explanations had been given. It was Faraday who first established the quantitative relationship between electricity and atomic weight in his two Laws of Electrolysis, put forward in 1834. These Laws state :—

(1) *For equal quantities of electricity, the amount of decomposition is constant, or the amount of decomposition caused in electrolysis is proportional to the quantity of current passed* (quantity of current is the current multiplied by the time for which it is passed, and is measured in coulombs, or ampère-seconds).

(2) *For the same quantities of electricity passed through different solutions, the amount of decomposition is proportional to the equivalent of the element, or group deposited.* Thus, if the same current is passed successively through solutions of copper sulphate, silver nitrate, and lead nitrate, as can easily be done by connecting the three cells in series, the amounts of the metals, copper, silver and lead deposited, will be in the ratio : 31·785 : 107·88 : 103·61. If the same amount of current is passed through solutions of ferrous and ferric sulphates, the amounts of iron deposited will be in the ratio 27·92 : 18·61.

Sidgwick has pointed out that actually these laws of electrolysis correspond exactly to the laws of constant and multiple proportions. We now believe that the current is carried through the solution by means of ions, which are charged atoms or groups. The above laws may be rewritten in more modern language: (1) the amount of electricity associated with an ion is constant; and (2) if an atom can form more than one type of ion (*e.g.*, ferrous and ferric, cuprous and cupric) then the amounts of electricity combined with the same atom bear a simple ratio to one another.

In the case of any electrolyte it follows from the first law that

$$W = Izt,$$

where W is the weight of substance liberated, I is the current, and t the time for which the current flows. z is a constant, called the *electro-chemical equivalent.* It is characteristic of each element or group.

From the second law it follows that one equivalent of any substance will be liberated by a certain quantity of electricity. This has been determined experimentally to be 96,500 coulombs ($\pm$ 0·01 per cent.), and is given the name of "the Faraday." It was found with great accuracy by Washburn and Bates in 1912, using the iodine coulometer. In this, the amount of electricity to liberate one equivalent of iodine was determined. Initially, the value of the Faraday was determined by the silver voltameter.

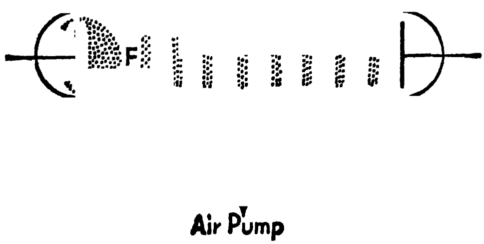
The value of the Faraday is an important physico-chemical constant, for, as we shall see later, we can calculate from it Avogadro's Number, *the number of molecules of a substance in a gram-molecule.*

Although it seems so clear, it is surprising that from 1834 until 1881 nobody noticed that if Faraday's Laws were true, then electricity, like matter, was not continuous, but discrete, being made up of small units. It was Helmholtz who first pointed this out in his famous Faraday Lecture, delivered before the Fellows of the Chemical Society, in London, on April 5th, 1881. He said: "Now the most startling result of Faraday's Laws is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

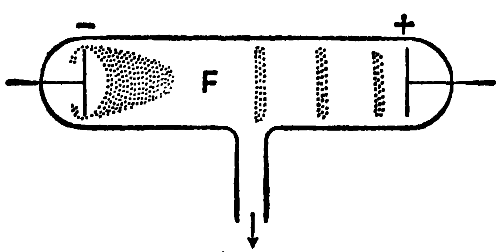
Thus was born the idea of the "electron"—the atom of electricity. Helmholtz did not use this term. It had, in fact, been stated by G. Johnstone Stoney in 1874, though not published until 1881, that "Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted upon. To make

this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases." The same person gave the name "electron" to this "single definite quantity of electricity" in 1891.

All this, however, had to do with electrolytes, *i.e.*, solutions of metallic salts in water, and it did not follow that this unit of electricity had anything whatever to do with the structure of matter. It must be clearly understood that Faraday's Laws lead only to the



Low Pressure.



Lower Pressure.

FIGS. 20 and 21.—Appearance of the Electric Discharge through a Gas.

conclusion that there exists a fundamental unit of electricity, and that this is in some way connected with valency, for a univalent ion bears one, a bivalent ion two, a tervalent ion three, and so on, of these units. It did not show at all that these units enter into the composition of the atom, as we now believe.

The next step in the unravelling of the structure of matter came from observations on the conduction of electricity by gases, and the study of radioactivity.

15. The Conduction of Electricity through Gases.—When a potential is applied to a gas such as air at ordinary atmospheric

pressure, the gas behaves as an insulator, and a negligible current passes. If, however, the pressure is reduced, a point is reached when the current flows, if the applied potential is sufficiently high, and the tube is filled with a glow—of a reddish purple colour in the case of air. This is what occurs in the ordinary Geissler tube. If the pressure is still further reduced the discharge becomes less symmetrical, a dark space, F (Fig. 20), appearing round the cathode. This is called the Faraday dark space, and is separated from the cathode by a bluish glow. Between the dark space and the anode is a series of striations, called the positive column. Still further reduction of pressure results in the formation of a new dark space immediately round the cathode, and the striations widen out. The state of the discharge in the two instances is shown in Figs. 20 and 21. The new dark space round the cathode is called the Crookes space. If the pressure is reduced to about 0·01 mm., the dark spaces and the cathode glow increase in size and the positive column

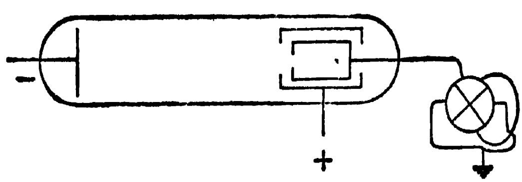


FIG. 22.—Apparatus to show the Nature of the Charge on the Cathode Particle.

gets smaller, and ultimately the Faraday dark space disappears, as it were, out of the end of the tube, as the positive column has done before it, so that the tube is now entirely occupied by the Crookes dark space and the cathode glow.

There are several things to be noticed about the Crookes dark space. It is always bounded by a luminous area. When the boundary is the gas in the tube the luminous area is the cathode glow, but when the dark space extends to the walls of the tube a bright fluorescence is produced. The colour of this fluorescence depends on the nature of the glass. If a metallic body is placed between the cathode and anode, it will cast a well-defined shadow on the walls of the tube, thus showing that whatever it is that produces this effect is travelling in straight lines. If a miniature paddle wheel is placed in the space, the wheel will rotate, thus showing that whatever is in this dark space will produce mechanical motion. These two facts together make it fairly clear that some sort of rays are present, and the name *cathode rays* is given to them.

The cathode rays will also produce heating effects ; if they strike any object placed in their path they may heat it to redness. If the rays are caught in a hollow metal box placed in the discharge tube, and connected through the wall of the tube to an electrometer (Fig. 22), it is found to gain a negative charge, so that whatever these rays may be, they are accompanied by a stream of negative electricity.

If an external magnetic field is applied to the discharge tube in which the discharge is passing, the cathode rays are deflected from their path in a direction at right angles both to their own path and to the direction of the lines of force of the field. This can readily be shown by passing the rays through a narrow slit, so that they pass along a zinc sulphide screen, in which they will produce fluorescence. The path of the rays is easily seen. On applying the field, usually by means of an electromagnet, the beam is seen to be bent. Considering the direction of the lines of force, and the direction in which deflection takes place, it follows from the usual

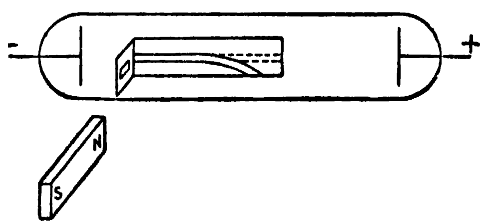


FIG. 23.—Arrangement of Apparatus to show the Deflection of Cathode Rays by a Magnetic Field.

rules governing the effect of a magnetic field on a current, that the rays consist of negatively charged particles, if, indeed, they are particles at all. An electrostatic field causes a deflection, but in a different direction. If a cathode particle is moving in the plane of the paper, and a magnetic field is applied with lines of force perpendicular to this plane, the cathode particle will be deflected at right angles to its original path, but still moves in the plane of the paper. When an electrostatic field is applied, with its lines of force perpendicular to the paper, the cathode particle is acted upon by a vertical force, which tends to lift it out of the plane.

The cathode rays will pass right through thin pieces of metal, the stopping power of the metal being proportional to the thickness and density. They will act as nuclei for the condensation of supersaturated vapours, causing fogs to be produced.

The nature of the cathode rays was for some time a matter of doubt. Crookes regarded them as a fourth state of matter, but it

was shown by Thomson, by means of experiments about to be described, that the ratio of the charge to the mass of the particle was the same irrespective of the nature of the gas in the tube. It was this observation that first indicated that the cathode rays are common constituents of all atoms.

The experiments of Thomson leave no doubt that the cathode particles are actually electrons.

Note on Electromagnetic and Electrostatic Units.—In this chapter we shall have occasion to use electrical units a good deal, and it is necessary to be thoroughly acquainted with the relationships that exist between the various systems in common use. There are two systems of *absolute* units—the *electrostatic* (abbreviated to e.s.u., and ultimately based on the force between two electric charges), and the *electromagnetic* (abbreviated to e.m.u., and ultimately based on the magnetic force due to a current). The absolute units are frequently too small or too large for everyday use, and a system of *practical* units is also used; the practical units are obtained from the corresponding absolute units by multiplying or dividing the latter by powers of 10.

Thus, the ampère and the volt are practical units, being respectively one-tenth of, and 10^8 times the corresponding absolute units on the electromagnetic system.

When the dimensions of the units on the two absolute systems are compared, it is found that the ratio of the electrostatic to the electromagnetic unit is a velocity, the reciprocal of a velocity, or the square of a velocity. Calculation reveals that this velocity is none other than the velocity of light, which is usually denoted by c, and is equal to 3×10^{10} cms. per second. In order to convert the electrostatic unit of current into the electromagnetic unit, it will be necessary to divide it by 3×10^{10}.

The Faraday is 96,500 coulombs. The coulomb is a practical unit, and it happens that to bring it to absolute e.m.u. it must be divided by 10. The Faraday is thus 9,650 e.m.u. To convert this into e.s.u., it must be multiplied by 3×10^{10}, giving $28{,}950 \times 10^{10}$ e.s.u., the value used on p. 67.

16. Determination of the Ratio of the Charge to the Mass of the Cathode Particle (e/m).—The determination of this ratio was one of the fundamental observations which paved the way for the modern theory of the structure of the atom. A knowledge of this constant enabled the charge of the electron to be arrived at.

It has already been mentioned that, since the cathode particles are charged negatively, they are deflected by magnetic and electric fields, and it was this behaviour that was used to obtain the ratio of the charge to their mass. First of all, it was possible to determine only the product of the velocity (v) of the particles and e/m. If a magnetic field of strength H is applied transversely to the direction of the rays, they are bent into a circle, the radius (r) of which can easily be determined by causing them to strike a zinc sulphide screen, in which they induce phosphorescence. Suppose the charge

on the cathode particle is e, and its mass m, the magnetic force acting on the particles, Hev, must be equal to the centrifugal force mv^2/r. Thus

$$\frac{mv^2}{r} = Hev,$$

or

$$\frac{m}{e} \cdot v = Hr.$$

The next matter was to discover v. It was thought that this velocity would be about the same as that of gas molecules as calculated by the kinetic theory (§ 75). This incorrect assumption led to a value of e/m which was roughly equal to the value obtained for the hydrogen ion in electrolysis, *i.e.*, 9,650 e.m.u.

Further methods were soon devised for determining e/m and v separately. In the first of these, the cathode particles were deflected by passing through a magnetic field, and were caught in an insulated metal box connected with an electrometer, of which the capacity was known. The rise in potential indicated by the electrometer in a given time was observed, thus giving the total charge, Q, on all the particles which were caught by the box. The total energy, W, of the particles was obtained by causing them to fall on a thermal junction placed inside the hollow box. If N is the number of particles collected in a given time, we have

$$Ne = Q, \quad (1)$$
$$N(\tfrac{1}{2}mv^2) = W, \quad (2)$$
$$\frac{mv}{e} = Hr.$$

Eliminating N,

$$v = \frac{2W}{QHr} \quad (4)$$
$$\frac{m}{e} = \frac{Q}{2W}(Hr)^2. \quad (5)$$

In this way the two values, that of the velocity of the rays and tha of the ratio of their charge to their mass, can be found. Th velocity was found to be about one-tenth that of light, and e/ about 10^7 e.m.u. This was about 1,000 times as great as the valu obtained for the hydrogen ion in electrolysis ; and so it was apparen that the cathode particles probably had small mass, but possesse comparatively high velocity. If it could be assumed that the charg associated with the cathode particle was the same as that carried b a univalent ion in electrolysis it would be possible to calculate m This assumption could not actually be verified until some time late when the charge on the cathode particle was determined separatel

If the assumption was true, the mass of the cathode particle was about one-thousandth of that of the hydrogen atom.

The second method of determining v and e/m separately depended upon the deflection of the rays by both a magnetic and an electric field. The apparatus employed is shown diagrammatically in Fig. 24. Cathode rays from C passed through the two slits A and B, which were earthed, and therefore served as anodes. They made the beam narrow. At the end of the tube was a fluorescent strip upon which the position of the beam was registered. An electric field was applied between the plates DD. This caused the rays to be deflected from their normal path, and the spot of light moved down the strip. Now, by applying a magnetic field between the plates DD, perpendicular to the path of the rays and parallel to the plane of the plates, the effect of the electric field can be annulled, since the

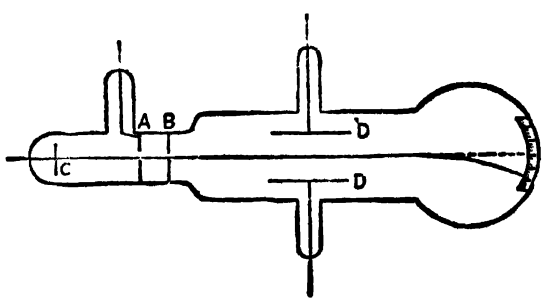


FIG. 24.—Apparatus for determining v and e/m of Cathode Particles.

magnetic and electric fields produce opposing deflections of the rays. The spot of light can thus be brought back to its original position. The strengths of electric and magnetic field necessary to do this are obtained. It then follows that, if X is the strength of the electric field, and the other symbols have their former significance,

$$Hev = Xe,$$

or

$$v = X/H.$$

The velocity of the particles thus determined was approximately the same as obtained in the previous determination. The value of e/m could now be determined by applying the magnetic field alone and determining the deflection. As before, this value came out to be about 10^7 e.m.u.

By varying the gas in the tube, and its pressure, it was found that the velocity of the cathode particles was dependent upon both these factors, but that e/m was unaffected by either alteration. This provided further proof that the cathode particles were constituents of all matter. Numerous other methods have been used for the

determination of e/m, and all confirm J. J. Thomson's result, $1{\cdot}77 \times 10^7$ e.m.u.

17. Positive Rays.—Since electrons are charged negatively they are driven away from the cathode in the discharge tube. There are, however, particles which travel towards the cathode from the anode. These eventually strike the cathode and were not discovered until a perforated cathode was used through which they could pass, and their properties could be investigated. For this reason these rays are sometimes called "canal rays," because they have passed through "canals," or perforations in the cathode. It is found that these rays can be deflected by means of a magnetic field, but the direction of deflection is opposite to that observed in the case of cathode rays, thus indicating that they bear a positive charge; the deflection is also smaller than with cathode rays for the same strength of field, indicating that the particles have a greater mass. These positive rays are of immense importance in elucidating atomic structure.

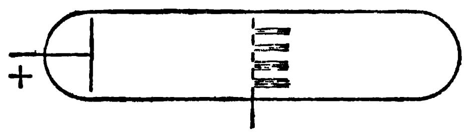


FIG. 25.—Production of Positive Rays.

18. X-rays.—When cathode rays strike any material object, a new radiation is given off, which has extraordinary powers of penetration, and will affect a photographic plate. For the production of these rays, which are called *X*-rays, a special tube is designed, a simple type of which is shown in the diagram (Fig. 26).

The tube consists of an ordinary discharge tube, which has been exhausted to such an extent that the Crookes dark space fills it. The cathode C is made of aluminium and is concave, thus causing the cathode rays to come to a focus at a point F, where they impinge on a piece of platinum arranged at an angle of 45° to the axis of the cathode, so that the *X*-radiation emitted at the impact is sent out of the tube. This piece of platinum, which is connected to the anode A, is called the anticathode.

A more modern type of *X*-ray tube is shown in Plate I. It has a water-cooled anticathode system, A, which is cemented to a glass tube, about 18 cm. long and 5 cm. diameter. The *X*-rays emerge from a window of thin aluminium foil ($\frac{1}{40}$ mm.) placed immediately in front of the anticathode. The cathode is a brass-sheathed aluminium rod, which passes through a cylindrical water jacket

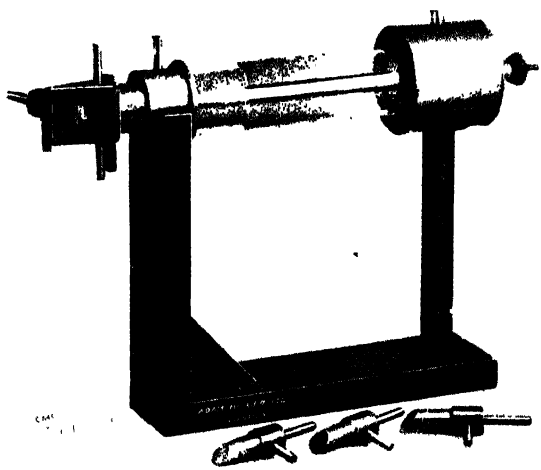


PLATE I. MODERN X-RAY TUBE.
(By permission of Messrs. Adam Hilger Ltd.)

[To face p. 60.

cemented to the glass tube. The length projecting down the tube can be adjusted so that the focus spot can be easily defined.

The X-rays will excite fluorescence in certain substances, and particularly in zinc sulphide and barium platinocyanide. When X-rays were first used for examination of bones, etc., it was always the fluorescence effect that was made use of, the shadow of the bones cast on a barium platinocyanide screen being examined. The photographic effect of X-rays has, however, proved much more convenient for this, as for most other X-ray work. It has the great advantage that long exposures of the affected parts are not required, thus preventing the risk of burning. Also, the X-ray photograph obtained can be studied at leisure, and in detail.

X-rays also have the remarkable power of enabling a gas to conduct electricity after it has been exposed to the rays. Thus, if an aluminium tube containing a gas, and with a wire running through it but insulated from it, is connected with a battery and an electrometer, as shown in Fig. 27, no current flows before the tube is irradiated with X-rays, but as soon as the rays are switched on, the gas becomes conducting.

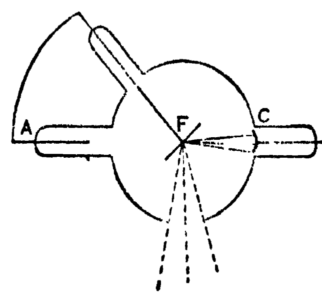


FIG. 26.—X-ray Tube (diagrammatic).

This is due to the fact that the passage of the X-rays ionises the gas, that is, it causes the gas atoms to become positively charged by the removal of electrons. This phenomenon of the ionisation of gases by means of X-rays is often used when it is necessary to render a gas conducting (as in Millikan's experiment, p. 70), and for providing nuclei for the condensation of supersaturated vapours (as in Wilson's experiments, p. 66).

X-rays were once considered to be pulses in the ether (*i.e.*, short groups of waves), but they are now known to be a wave motion of extremely small wavelength, about 10^{-8} cm. The wavelength of sodium light is about 5,890 Ångstrom units, one Ångstrom unit being 10^{-8} cm., so that X-rays have a wavelength roughly 5,000 times smaller than that of visible light. The wavelength of the X-rays emitted from any tube depends upon the nature of the anticathode. It has been determined by studying the interference of the rays when they fall on a crystal, which acts as a three-dimensional grating for them, just as a diffraction grating is used in optics to determine the wavelength of light. The method of carrying out

this experiment is described in the chapter on the Crystalline State (§ 125). One of the most important uses to which X-rays have been put is the study of crystalline structure.

When X-rays strike other bodies, other X-rays are emitted from these bodies, called secondary rays, whilst some are diffusely reflected. The secondary rays are made up of two groups: the "K Series," which are of shorter wavelength, and are penetrating, and are called "hard" rays; and the "L Series," which are softer, of longer wavelength, and not so penetrating. The wavelengths of secondary rays are determined by the element on which the impingement takes place, being governed by the atomic number of the element according to a relationship to be discussed later (§ 34). The study of these secondary rays has provided a most important method of deciding atomic structure, and particularly of discovering the number of electrons present in the atom outside the nucleus.

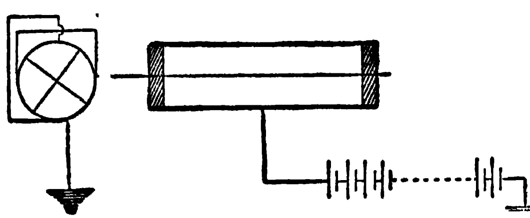


FIG. 27.—Apparatus to show Ionisation of a Gas by X-rays.

*19. **Radioactivity.**—Shortly after Röntgen's discovery of X-rays in 1895, Becquerel discovered that photographic plates which had been placed near uranium salts were fogged, showing that some penetrating radiation which could affect the plate was emitted by these compounds. The rays were found to be very similar to X-rays in their properties, as they would also ionise gases, and induce phosphorescence in certain substances. They were not affected by heat, light or chemical combination. No matter what uranium compound was used the activity was still present.

Two years later, Mme. Curie found that thorium compounds acted similarly, and investigated also other uranium minerals. Some of these, she found, were more active than uranium itself, so that they must contain a more active element or compound. After a long process of chemical separation, she isolated two other elements which had a much greater activity than uranium. These she called polonium, an element related in chemical properties to tellurium, and radium, which behaves chemically like barium.

Other investigators took up the study of radioactive minerals, and in 1900 another element, actinium, was discovered by Debierne and Giesel.

The sources of uranium and radium salts are minerals, such as pitchblende (which was shown by Klaproth to be an oxide of uranium, U_3O_8), containing a very small amount of radium, and carnotite, a vanadate of potassium and uranium. The latter contains also some radium, and is an important source of the metal. It is much more difficult to obtain radium from mineral sources than it is to get uranium, although radium is always associated with uranium in very small proportions (about 1 gm. of radium in 3 tons of uranium). Uranium salts are comparatively cheap, whilst, of course, radium is the most costly of metals. Unfortunately, the radiation from uranium is not medically active, or at any rate is not sufficiently strong to act in an appreciable time, that of radium being 1,000,000 times as active.

The separation of radium from minerals is a very laborious process, depending upon repeated fractional crystallisation. (To obtain it from carnotite, the mineral is heated to 190° C. with about 80 per cent. sulphuric acid; the solution is filtered through glass wool, when, on cooling, it deposits radium and barium sulphates. Radium is a metal of Group II. in the Periodic Table, and resembles barium. Consequently its sulphate is insoluble in water, being, as would be expected, even less soluble than barium sulphate. Both are, however, soluble to a limited extent in strong sulphuric acid, the acid sulphates (*e.g.*, $Ba(HSO_4)_2$) being formed. Hence the method adopted for the separation. The sulphates are now reduced to sulphides by heating with carbon, and the sulphides are treated with hydrobromic acid to convert them into bromides. The solution is then crystallised. Eight fractional crystallisations are usually sufficient to effect complete separation.)

Radium is a white metal like barium. The salts resemble those of barium in almost every respect, but in solution oxygen and hydrogen are given off continuously. The dry salts will ozonise air, and in the dark they phosphoresce.

20. Nature and Characteristics of the Radiation from Radioactive Substances.—The radiation emitted from radioactive substances has been shown to consist of three types, which are named α-, β- and γ-rays, and which differ considerably in their nature. They have different penetrating and ionising powers. The α-rays have the lowest penetrating power. The distance they will travel is called their *range*. Whilst they will travel for distances of about 7 cm. in air at atmospheric pressure, they are soon stopped by any solid body, such as a sheet of paper. β-Rays are much more penetrating,

and will pass through thin sheets of metal. As for X-rays, the more dense the metal, the greater is its stopping power, and so it is found that β-rays are stopped by lead of greater thickness than about 3 mm. γ-Rays are still more powerfully penetrating, passing through 6 inches of lead.

The nature of these radiations has been elucidated by studying the action of magnetic and electric fields upon them. The effect of a magnetic field on these radiations is shown in Fig. 28. Here it is seen that the effect on α-rays is opposite to that on β-rays, showing that they are opposite in charge. The effect, too, is greater upon β-rays than it is upon α-rays, as can be seen by the greater curvature

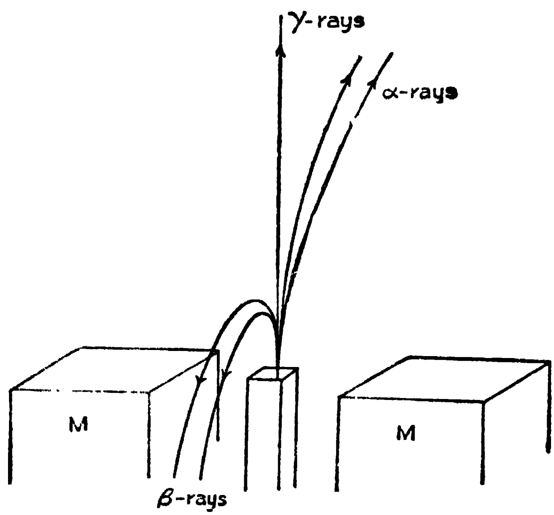


FIG. 28.—The effect of a Magnetic Field on α, β and γ-rays.

in the former case. This means that the α-rays have considerably greater mass than β-rays. The γ-rays are quite unaffected by a magnetic field, indicating that they do not possess any electric charge at all. It has been shown that these rays are actually similar in nature to X-rays, but as a rule, have even shorter wavelength. Their wavelength, however, varies, and some γ-rays possess wavelengths of the same order as those of X-rays.

21. α-Rays.—The elucidation of the nature of α-rays was one of the early achievements of Lord Rutherford. He showed that they were positively charged particles, and by determining the ratio of the charge to the mass by a method similar to that used for cathode rays, he showed that their e/m value was 48,230 coulombs per gram.

It will be remembered that for the liberation of 1 gm. of hydrogen in electrolysis 96,500 coulombs were required, so that this value is just half that for the hydrogen ion. The α-rays were thus particles which were positively charged and had masses of the order of atomic mass. There are several possibilities: the rays may consist of singly charged atoms with mass 2, or of atoms of mass 4, bearing two positive charges, atoms of mass 6, triply charged, and so on. If they were doubly charged atoms of mass 4, they would consist of helium atoms bearing two positive charges, *i.e.*, the helium nucleus (§§ 29, 32).

This last view was proved to be correct by direct experiment. Rutherford and Royds sealed up some radium emanation (see p. 80) in a thin glass tube so that the α-rays could get through the walls. This was placed in an outer evacuated tube fitted with electrodes. On passing the discharge, the spectrum of helium was obtained.

This could be confirmed by determining the charge on the α-particle, and then calculating the mass m from the ratio e/m. There are several ways in which this can be done. When α-rays fall on a zinc sulphide screen they cause phosphorescence, each α-particle causing a definite flash. This has been made use of in the spinthariscope, an instrument described on p. 202, in connection with the determination of Avogadro's Number. It is there described how the α-particles can be counted by noting the number of flashes in a given time. Rutherford determined the number of α-particles falling on a given surface in a given time, and also, in another experiment in which the zinc sulphide screen was replaced by a metal screen, the charge imparted to the latter in the same time. He was thus able to calculate the charge associated with each α-particle, and this came out to be $9{\cdot}3 \times 10^{-10}$ electrostatic units, which is just twice the charge on a hydrogen ion. Since e/m for the α-particle is one-half that for the hydrogen ion, the mass of the α-particle must be four times that of the hydrogen ion, *i.e.*, its mass corresponds to that of the helium atom. The α-particle must therefore be the helium atom bearing two positive charges, or the helium atom less two electrons.

Since the α-particle is emitted with high velocity, and its mass is comparatively large, it possesses considerable kinetic energy, and hence in its passage it is able to pass right through atoms [the explanation of this point will be clear after reading the section on the nuclear theory (§ 29)] with practically no deviation, until its energy becomes spent. Towards the end of its path it may be reflected by coming into contact with the electric field of an atom, and this process of scattering of α-rays in gases proved to be the clue which enabled Rutherford to give a picture of the atom.

The actual path of α-particles through gases has been photographed by the ingenious method originally due to C. T. R. Wilson. When the rays pass through a gas, they ionise it, and the ions formed can then act as nuclei for the condensation of supersaturated vapours. If air, saturated with water vapour and perfectly free from dust is suddenly cooled, no water droplets settle out; the air simply becomes supersaturated with water vapour. If now a radioactive source emitting α-rays is placed in or near the vessel, the paths of the α-rays through the gas are made evident by a line of water droplets, which can be photographed if the vessel is illuminated. The photographs of α-ray tracks obtained in this way (Plate II.) indicate that α-rays pursue a straight course until very near the end of their tracks, when there may be a deviation from the path, which shortly afterwards ends suddenly. Where the deviation occurs, there is a slight spur, which is due to the recoil of the atom which has collided with the α-particle, and from the direction of this spur and that of the α-particle, the relative masses of the atoms can be calculated to a rough degree of accuracy.

The tracks of α-rays which can thus be made evident to our senses provide a proof of the existence of single atoms. In watching the track of an α-ray we are really watching the motion of a single charged atom.

22. β-Rays.—β-Rays are more penetrating than α-rays, and are also lighter. They move with a much greater velocity, and have been shown to consist of electrons. The mass of an electron of low velocity is about 1/1,850 that of the hydrogen atom, as has been shown by the experiments on determination of e/m for cathode rays, and of e. This mass is, however, dependent upon the velocity with which the electron is moving According to the theory of relativity the mass of a moving electron becomes infinite when its speed is that of light, and is given, for any other speed, by the equation

$$m = m_0 \left[1 - \left(\frac{v}{c}\right)^2\right]^{-\frac{1}{2}},$$

where m_0 is the mass when the electron is stationary, m is the mass at velocity v, and c is the velocity of light. The β-particles shot off from radioactive sources have various velocities, but those from radium C have velocities approaching that of light.

The β-particle has a small mass compared with that of an α-particle and consequently possesses much less kinetic energy. It cannot, therefore, cause such extensive ionisation as the α-particle, and is more easily deflected by electric and magnetic fields whether these be applied externally, or whether they be due to atoms in the path of the particle. In consequence, it follows a much more devious path through a gas, as has been shown by the cloud method.

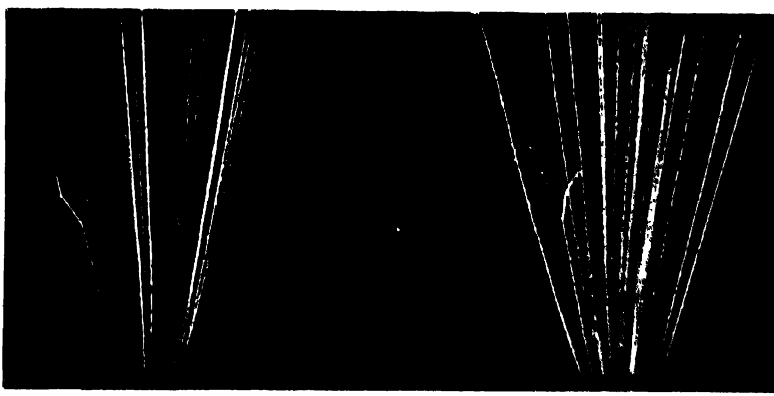


PLATE II.—TRACKS OF α-PARTICLES.

On the left a particle is deflected by collision with a molecule, on the right a particle has collided with a nitrogen atom, driving out of it a proton. (From Andrade's *Structure of the Atom*, by permission of Messrs. G. Bell & Sons.)

[*To face p.* 66.

23. γ-Rays.—These, as has already been explained, partake of the nature of X-rays, being extremely penetrating. The wavelength varies with the source. If the wavelength is long enough, it is possible to determine it by interference at crystal faces, just as the wavelength of X-rays is determined (§ 125), but in some cases the wavelength is too small for even a crystal lattice to act as a grating.

24. Secondary Radiation.—In dealing with X-rays it was mentioned that when this radiation comes into contact with other matter, the latter itself gives off X-rays, which are called the secondary radiation. The same thing happens when any of the radioactive radiations strike matter. In general, the secondary radiation is much weaker than the radiation which caused it. γ-rays may produce secondary β-rays, and α-rays may produce both β- and γ-rays. When α-rays are absorbed by matter, a new type of radiation, called δ-rays, is also produced. These are soft β-rays, *i.e.*, electrons with small velocities.

25. Recoil Atoms.—When an α-particle is emitted from a radioactive source, it follows, from the principles of mechanics, that the atom from which the α-particle has been shot must recoil, just as recoil occurs when a rifle is fired. The velocity of recoil is governed by the ordinary principle that the sum of the momenta of the two particles is constant. As radioactive atoms are usually very heavy, having atomic weights about 200, it follows that the recoil velocity will be considerably smaller than the velocity of emission. It will, in fact, be about 1/50th of the latter. This velocity, however, is sufficient to enable the recoil atom to possess the power of causing ionisation. The difference between an α-particle and the recoil atom lies in its range. The α-particle, possessing the greater velocity, will go further than the recoil atom. The recoil atoms therefore act like α-particles which have approached the end of their range.

Recoil may also occur when a β-particle is emitted, but it does not appear that the recoil atom in this case is capable of causing ionisation.

26. Determination of the Charge on the Electron.—Faraday's experiments on electrolysis showed that 1 gm. equivalent of any substance is liberated by the passage of 96,500 coulombs of electricity through the solution. Now, if the substance concerned forms a univalent ion, the equivalent is the same as the molecular weight, so that one gram-molecule of a univalent ion is liberated by 96,500 coulombs, or 9,650 e.m.u. This is equal to $28{,}950 \times 10^{10}$ e.s.u. (see the section on electromagnetic and electrostatic units, p. 57). If n is the number of molecules in 1 c.c. of a gas at N.T.P., one gram-molecule of a substance contains 22,400 n molecules, in whatever state it

is. Hence, the charge, e, on one univalent ion must be $28{,}950 \times 10^{10}/22{,}400\ n$ e.s.u., or the product, ne, is equal to $1{\cdot}24 \times 10^{10}$ e.s.u. If we could determine n, we could find the charge on the ion, which we could assume was equal to the charge on the electron; but neither of these quantities can be deduced separately from electrolysis experiments, and in the early attempts to determine e, approximate values of n were used. All that was known about n before the magnitude of the electronic charge was determined was that it lay between 10^{18} and 10^{21}, and hence the value of e was quite uncertain.

The first experiments on the determination of the electronic charge were made by Townsend, and have served as the basis of the most accurate methods of Millikan. It is therefore important to study the history of the methods of carrying out this work.

1. When newly prepared gases are bubbled through water, electrically charged clouds are formed in many cases. Townsend thought of the idea of determining the charge on a drop in such a cloud, which he assumed to be the charge on the electron. Townsend prepared a cloud, using gases obtained by electrolysis. By means of a quadrant electrometer, the total electric charge per c.c. of gas was determined, and the total weight of the cloud was found by absorbing it in drying tubes and finding the increase in weight. To determine the average charge of a drop, it was necessary to find the weight of one drop, and this was done by finding the rate of fall of the cloud under gravity, and applying Stokes' Law for the velocity of a sphere, moving slowly through a viscous medium, under the action of a constant force. It states that

$$v = 2ga^2\sigma/9\eta,$$

where v is the velocity of the drop under gravity g, a is the radius, σ the density of the drop, and η the viscosity of air.

He could thus calculate the number of drops, and knowing the total charge, and assuming that each drop bore one charge, he was able to determine the charge on each particle. This came out to be 3×10^{-10} e.s.u. After allowing for the fact that some of the drops in the cloud were charged differently, he gave the corrected value $e = 5 \times 10^{-10}$ e.s.u.

2. Shortly after the publication of this experiment, Sir J. J. Thomson used the same method to determine the charge on the ions produced in a gas by the passage of X-rays through it. A cloud was formed as in C. T. R. Wilson's experiments, by sudden expansion and resulting cooling of the air, causing the water vapour to condense on the ions. The apparatus is shown in Fig. 29.

The sudden expansion is brought about by pulling down the

piston P. The weight of the cloud produced was determined indirectly, by calculation, from the amount of cooling produced, and the densities of saturated water vapour at room temperature and at the lower temperature caused by the expansion. The total charge per c.c. was determined by finding the conductivity of the cloud, measuring the current which flowed when a small electromotive force was applied between the aluminium cap to the vessel A, and the surface of the water. The size of the drops was determined, as before, by applying Stokes' Law. The values $6{\cdot}5 \times 10^{-10}$ e.s.u., and $6{\cdot}7 \times 10^{-10}$ e.s.u. were found for the charge on a drop in air, and in hydrogen, respectively. Later, Thomson obtained the value $6{\cdot}8 \times 10^{-10}$ e.s.u. for negative ions generated by the action of ultraviolet light. In a later experiment, which he thought to be more

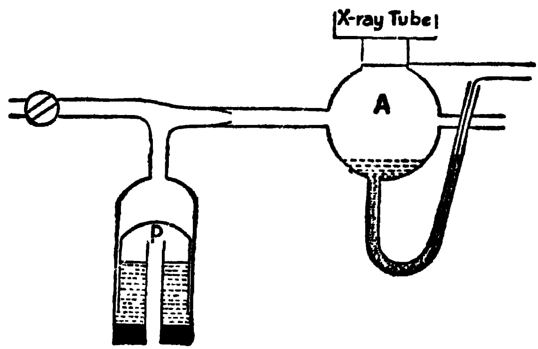


FIG. 29.—Sir J. J. Thomson's Apparatus for determining the charge on the electron (1898).

accurate, he obtained the value $3{\cdot}4 \times 10^{-10}$ e.s.u., using in this case a radioactive source for the ions.

These determinations of Thomson and Townsend were extremely difficult to carry out, and contained numerous sources of inaccuracy. Also, it must be remembered that in all cases it was assumed that each drop was charged with only one elementary charge. That this assumption is very questionable will be clear when the work of Millikan is considered. With his apparatus Millikan was able to obtain oil drops with almost any number of charges. There was also the difficulty that had to be cleared up, as to whether the charge on these drops was the same as the charge on a univalent ion in electrolysis. Once this had been established, it was possible to find out the size of the charge on the cathode particle, and its mass.

The identity of the charge on the electron and that on a univalent ion was demonstrated by Townsend in 1899. He proved that if e is

the charge on an ion in a gas, U its mean velocity in the direction of an electric force Z, and K the coefficient of diffusion of the ions,

$$U/K = neZ/P$$

P being the pressure of the gas, which contains n molecules per c.c., at the temperature of the experiment.

Townsend then determined the coefficient of diffusion of the ions, and, taking the corresponding values of U which had been determined by Rutherford, he obtained the following values of ne (e.s.u.) :—

Air	$1{\cdot}35 \times 10^{-10}$
Oxygen	$1{\cdot}25 \times 10^{-10}$
Hydrogen	$1{\cdot}0 \times 10^{-10}$
Carbon dioxide	$1{\cdot}30 \times 10^{-10}$

The value of the charge on an univalent ion in electrolysis multiplied by the number of ions equal to the number of molecules in 1 c.c. of gas at N.T.P. is $1{\cdot}24 \times 10^{-10}$ e.s.u. These figures are sufficiently close to the electrolytic value, then, to enable the conclusion to be drawn, that the charge on a gaseous ion is equal to that on an univalent ion present in electrolysis, and this has been confirmed by numerous other experiments.

The next development was an improvement made in Thomson's apparatus by H. A. Wilson. The object of it was to avoid the difficulty, already referred to, of the uncertainty as to the number of charges carried by an ion. Two brass plates were fixed in the expansion chamber, A, of Thomson's apparatus, so that a vertical electric field could be applied. It was then possible to aid or hinder the action of gravity on a drop by altering the sign of the electric field. The weight of the drop was determined by the usual application of Stokes' Law, the rate of fall of the drop under gravity alone being determined. The charge was determined by finding the change in velocity when the electric field was put on to assist the action of gravity. The change in velocity was found to be not the same for all drops, the cloud being made up of drops which bore charges in the ratio 1 : 2 : 3.

This important conclusion made it evident that this was a source of inaccuracy in the earlier determinations, though Wilson himself obtained a value $3{\cdot}1 \times 10^{-10}$ by this method. The idea of using a controlling electric field was worked upon by Millikan, in America, his experiments extending over a period of eight years (1909–16).

Millikan, realising the inaccuracy due to the rapid evaporation of water drops, used instead, drops of a non-volatile oil. He also employed a much higher field strength, and was therefore able to keep the drop suspended between the plates, or could make it rise or fall at will.

His apparatus is shown in Fig. 30. The oil drops were introduced into the cylindrical vessel V, by means of an atomiser A, resembling somewhat in action a carburetter of a motor car. The brass plates, B and C, were connected, one to the pole of a battery of accumulators, of total voltage 10,000 volts, to maintain a steady high potential, and the other to earth through the vessel. The vessel V was placed in a thermostat to keep it at constant temperature.

The top plate had a pin-hole through which drops of oil occasionally found their way. The drops were already charged by the

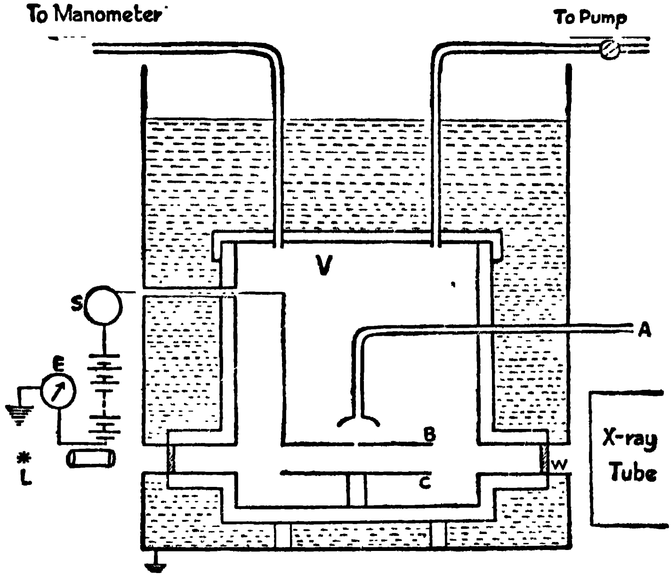


FIG. 30.—Millikan's Apparatus (diagrammatic).

friction of the atomiser, but they could be further charged by ionising the gas in the vessel by means of X-rays which were shone through a window, W. The drops which had passed between the plates were illuminated by a powerful source of light, L, and viewed through a telescope. Any heat rays were removed from the light by passing it through filters, so that its entry to the chamber did not upset the motion of the drops by currents. The pressure in the chamber, which could readily be altered, was indicated by a manometer. In the telescope eyepiece was a scale which enabled the position of the drop to be gauged to a great degree of accuracy, and the times were recorded to thousandths of a second by means of a chronograph. E was a voltmeter for measuring the potential of the battery.

The drop, which was positively charged by friction, entered the space between the plates, and then the electric field was applied so that it was attracted towards the upper plate B. Just before it got there, the plates were short-circuited by the switch S, and the drop was allowed to fall under gravity until it got almost to C, when the field was put on, and it was dragged up again. The drop could thus be made to rise or fall continuously, and the attainment of another charge was immediately shown by a change in the velocity. The times taken for the drop to fall alone under gravity, and to rise under the action of the field, were found. The time taken for a drop to fall a distance of 0·5222 cm. was 13·595 sec., the maximum deviation in seventeen experiments being only $\pm$ 0·2 sec. On the other hand, the times taken for the drop to rise under the action of the field (5,051 volts) varied considerably, as is shown by the following numbers, which represent the times in seconds taken for the upward journey on successive occasions: 12·5, 12·4, 21·8, 34·8, 84·5, 84·5, 85·5, 34·6, 34·8 secs.

It is clear that on the third journey up, the drop had taken up another negative ion, on the next journey another, and on the next, another. If v_1 is the velocity under gravity alone, and v_2 the velocity under gravity and the field of strength X, and e is the charge on the drop of mass m_a, then

$$\frac{v_1}{v_2} = \frac{m_a g}{Xe - m_a g} \quad ; \quad e = \frac{m_a g}{Xv_1}(v_1 + v_2).$$

The change in velocity consequent upon the drop taking up an additional charge, can be obtained from the equations

$$e = \frac{m_a g}{Xv_1}(v_1 + v_2),$$

$$e + 1 = \frac{m_a g}{Xv_1}(v_1 + v_3),$$

where v_3 is the velocity after taking up an additional charge.

With the figures mentioned above,

$$\text{when } t = 34{\cdot}8 \text{ secs., } v_1 + v_2 = \frac{0{\cdot}5222}{13{\cdot}595} + \frac{0{\cdot}5222}{34{\cdot}8} \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$\text{when } t = 84{\cdot}5 \text{ secs., } v_1 + v_3 = \frac{0{\cdot}5222}{13{\cdot}595} + \frac{0{\cdot}5222}{84{\cdot}5} \quad . \; . \; . \; . \; . \; . \quad (2)$$

∴ The difference between (1) and (2)

$$= 0{\cdot}5222\left(\frac{1}{34{\cdot}8} - \frac{1}{84{\cdot}5}\right) = {\cdot}00891 \text{ cm./sec.}$$

In this way it was found that the successive capture of a single charge by the drop gave rise to differences in its velocity equal to 0·008912, 0·008911, 0·008903, 0·008883, and 0·008931 cm. per sec.,

giving a mean value of 0·00891 cm. per sec. It will be seen that the individual results do not differ very greatly from this mean value.

The fact that relationships of this sort were obtained always, irrespective of the nature of the gas in the vessel, or its pressure, or how long the experiment was being conducted, indicates without the faintest doubt that the charges on ions are all the same in value, or are multiples of some fundamental value. This is the best proof of the atomic nature of electricity.

From the above equations, the ratio e/m_a for the droplets could be found. To determine e, it is now necessary to find m_a. This can be done by applying Stokes' Law (§ 26), but Millikan showed that whilst the Law was true for particles of considerable size, for particles of the size of these droplets it ceased to be more than approximately true. He therefore devised a more accurate form of Stokes' Law which would apply to these particles. By this means he was able to find m_a with a degree of accuracy comparable to that obtainable in the rest of the experiment. Finally, his value for e was $(4{\cdot}774 \pm 0{\cdot}005) \times 10^{-10}$ e.s.u.

Several means of ionisation were employed, and in every case the same result was obtained.

The fact that e has been determined with great exactness enables the value of the Avogadro Number, the number of molecules in a gram-molecule of any substance, to be determined with accuracy. In electrolysis it is found that one gram-molecule of a univalent substance is liberated by 9,650 e.m.u. of electricity. This is equal to $28{,}950 \times 10^{10}$ e.s.u. This is equal to Ne, the number of molecules in a gram-molecule multiplied by the charge on an ion. Thus, if we divide this figure by the charge (e) determined by Millikan, we should arrive at Avogadro's Number (N); this comes out to be $6{\cdot}062 \pm 0{\cdot}006 \times 10^{23}$. (For further methods of finding Avogadro's number, see § 79.)

The result of the most recent determination of the charge of the electron (Hopper and Laby, 1941) determined by the oil-drop method is $(4{\cdot}802 \pm 0{\cdot}001) \times 10^{-10}$ e.s.u. This value agrees with that obtained by Bearden (1941) by the X-ray method.

27. Sir J. J. Thomson's Theory of the Structure of the Atom.— The experiments already described show without doubt that the electron is an integral part of all matter. The cathode rays emitted from all types of matter have the same elementary charge, and the ions produced by all gases possess this charge or else some simple multiple of it. The electron is, therefore, to be found in the atom. All chemical atoms, in the ordinary state, are, however, electrically neutral, and hence there must be some positive charge somewhere

in the atom to neutralise the negative charge of the electrons. The nature of this positive charge was not known when the experiments on the determination of e/m for cathode rays were done, and the existence of the electron defined.

Sir J. J. Thomson assumed that the electrons moved in " a sphere of positive electrification." This, of course, was pure hypothesis. By considering the positions taken up by magnetic poles placed in a magnetic field, Thomson showed that the electrons would arrange themselves in rings of eight, which suggested the periodic recurrence of properties in the elements as the atomic weight increases, and thus fitted in with the Mendeléeff Periodic Table (§ 11), which was based on the Law of Octaves. It certainly seemed that the number eight was a magic number as far as the atom was concerned. This arrangement of electrons was later shown to be essentially correct, though by a somewhat different theory.

28. The Bombardment of Matter by α- and β-Rays.—It has already been shown that the β-rays emitted from radioactive substances are electrons moving with various velocities, in many cases high velocities somewhere in the neighbourhood of the speed of light. If matter is bombarded by these small particles, their resultant deflections should give us some information concerning the electrical state of the atoms in matter.

If a parallel beam of β-rays from some radioactive source is passed through a thin metal sheet, such as a piece of aluminium foil, or gold leaf, the beam emerges divergent. This is due to the repulsion of the β-particles by the electrons in the atom, which possess the same electrical sign. From the amount of the divergence, the number of electrons in the atom of the metal can be found. This comes out, as a rule, to about half the atomic weight. Thus, for aluminium it is 13, whilst the atomic weight of aluminium is 27; for sodium it is 11, the atomic weight of this element being 23. Now the mass of the electron can be determined, since we know e/m, and we know e. Its mass is very small indeed. Since an atom like aluminium contains only 13 of these, the proportion of the mass of the atom due to the electrons is very small. The electron has a mass of about $\frac{1}{1850}$ that of the hydrogen atom, so the 13 electrons will weigh about $\frac{13}{1850}$ units. The ratio of this to the total mass of the atom is $\frac{13}{27 \times 1{,}850} = \frac{1}{38{,}430}$. Hence there must be some other part of the atom which possesses most of the mass, and since the atom is supposed to be made up of nothing but electricity, it follows that the mass is concentrated in the positive part of the atom.

This view was to receive considerable support from the study of

the bombardment of matter by α-particles These are small, positively charged particles, and are much heavier than β-particles. They will therefore be more effective in bombardment (see § 42).

Geiger and Marsden studied the result of bombarding a piece of gold foil with α-particles from a radioactive source. Some of the particles were deflected slightly from their course, some were scattered through larger angles, and some were actually deflected right back. The number which suffered a deflection of about 180° was, however, very small, being only about 1 in 20,000. The average scattering was 0·87°, showing how few suffered anything but a very small deflection. It might be thought that those particles which were directly reversed in direction were merely reflected from the surface of the gold leaf, but this is not so, since the number of particles which undergo large deflections is proportional, within certain limits, to the thickness of the gold foil. It is, therefore, some phenomenon connected with scattering in the interior of the metal. What is it that causes these α-particles to suffer such large deflections ?

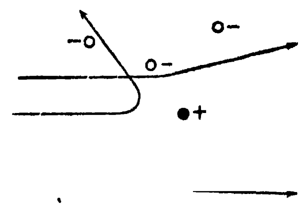


FIG. 31.—The scattering of α-Particles at Electrons and Protons.

29. The Nuclear Theory of Rutherford.—It was these data which furnished Rutherford with the material upon which to base the nuclear theory of the atom, which, although modified and extended, forms the basis of all modern work on subatomic physics.

The α-particle is about 7,000 times as heavy as the electron, so that it will be hardly moved out of its course at all by coming into contact with one of them. As it is turned back through such large angles, it must be colliding with something of about its own mass and charge. Rutherford pointed out that if Thomson's "sphere of positive electrification" were condensed into a small nucleus, the particle necessary to cause these deflections of the α-rays was present. On this basis, Rutherford calculated, from the values of the scattering of α-particles, the number of charges there must be on the positive sphere, and found it to be equal to about half the atomic weight. The charge on the positive sphere, or nucleus, was the same as the total charge on the extra-nuclear electrons in the atom which had been determined by observation of the scattering of β-rays, and later of X-rays. There can therefore be only one of these centres in each atom, otherwise the atom would be positively charged.

Rutherford's theory is that the atom is made up of (1) a positive

nucleus, which is small, but which possesses the major part of the mass of the atom; and (2) a number of negative electrons, equal to the number of net positive charges on the nucleus.

It is clear that if these electrons are stationary, there is no reason whatever why they should not be attracted by the nucleus, and fall into it. In order to avoid this difficulty (which was not present in the Thomson model) it was assumed that the electrons moved in orbits round the positive nucleus, being kept from falling into it by the centrifugal force which was always acting outwards.

The atom has often been likened to a solar system in miniature. The positive nucleus is the sun, the electrons are the planets. If the planets were not in motion round the sun, they would immediately fall into it; but as they are in motion in orbits, the centrifugal force prevents them from being drawn in. This simple picture of the atom has provided us with a very satisfactory method of explaining many facts, and it is now believed to represent, fundamentally, the state of affairs obtaining in the atom, though certain refinements in theory have been made which will be described later.

It may, however, be stated here that there is a difficulty with this simple theory. Niels Bohr showed that such an atom would be unstable, and modified the model by supposing that the electrons could only move in certain definite orbits (§ 46).

***30. Protons, Electrons and Neutrons.**—The name given to the heavy particle bearing one positive charge only, is the *proton*. The hydrogen atom, being the lightest atom, must contain the lightest nucleus, and it is known that it has one extra-nuclear electron. It is possible to obtain, in a suitable discharge tube, positive rays which consist of hydrogen atoms which have been deprived of their electrons, and which therefore consist of a nucleus bearing one positive charge.

The proton is much heavier than the electron, accounting as it does for nearly all the mass of the atom; but it cannot be a very large particle, because so few α-particles are deflected through large angles when matter is bombarded with them. It will be remembered that the total average scattering was only 0·87°, showing that the vast majority of α-particles merely grazed the nucleus, being deflected but slightly by it, whilst very few hit the nucleus head on, and were returned along the path they had come, or nearly so. This means that the spaces in the atom are very large, it being possible for an α-particle, which we know to consist of the helium nucleus, to get right through without hitting anything. In a sheet of aluminium foil, the α-particle may go through thousands of atoms without suffering collision.

In this respect the atom again resembles the solar system. In

the latter, by far the greater part of the system consists of empty space, and shooting stars can pass right through it without colliding with anything. The α-particle in the scattering experiments can be likened to a shooting star. It may pass through the atom without hitting anything ; on the other hand, it may collide with a nucleus, though the chances of its doing so are small.

The mass of the electron is about 1/1,850 of that of the hydrogen atom, as has already been shown, so that it is also about that fraction of the mass of the proton.

It should be mentioned that a particle bearing one positive charge, yet possessing a mass much smaller than that of the proton, comparable, indeed, with that of the electron, has also been discovered, and is called the positive electron or positron (§ 43).

When beryllium, and certain other light elements such as lithium and boron, are bombarded with energetic α-rays from polonium, a very penetrating radiation is emitted. This was discovered by Bothe and Becker in Germany in 1930, who thought at first that it was a very penetrating α-radiation. In 1932, Curie and Joliot showed that this radiation was capable of expelling high-energy protons from paraffin wax, and later in that year Chadwick determined the number and range of these protons. The results he obtained were inconsistent with the view that the incident radiation was simply a form of α-ray, and he showed that it was, in fact, composed of uncharged particles with a mass approximately that of the proton. These particles are called *neutrons*, and are considered to be present in the nuclei of all atoms except hydrogen. The mass of the neutron was determined by Chadwick and Goldhaber in 1939 to be 1·00895 on the basis O = 16.

31. Radioactive Disintegration.—We are now in a position to study the products of radioactive disintegration, *i.e.*, the products obtained from radioactive substances when α-rays and β-particles are emitted. These products, starting from uranium, actinium and thorium respectively, are given, together with the half-life values of the elements, in Tables IV., V. and VI.

This term requires a little explanation. The rate of decay of any radioactive substance is an exponential function, depending upon the amount of the substance left. It is like a geometrical progression. To take a hypothetical example, suppose that half of the actual amount of a substance present disintegrated each day. At the end of the first day there would be one-half left, at the end of the second one-quarter, at the end of the third one-eighth, and so on. The series is infinite. Actually the substance would never disintegrate completely. So it is with all these radioactive elements. The rate of decay depends upon the amount of substance present, and

so no element actually decays away completely, though its concentration may become so small as to be immeasurable. It is therefore useless to take the time of complete disintegration of an element in order to characterise it, for this would be infinity for all of them. The value taken is, then, the half-life period, *i.e.*, the time taken for the element to become half disintegrated. When we say that the half-life period, or, more simply, the period of radium is 1,590 years, we mean that if we start with 1 gm. of radium, by the end of this period it will be reduced to ½ gm. of radium, and some other products. The various radiations emitted are also shown in these tables.

It is seen that when an α-particle is emitted by an element, the latter is converted into an element two places to the left in the Periodic Table. Radium in Group II. loses an α-particle, and becomes radon, or radium emanation, a gas of the inert gas series, Group 0. When an element loses a β-particle it changes to one occupying one

TABLE IV.—THE ACTINUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. N
Uranium ?	—	α	—	VI.	92
Uranium Y	UY ↓	β	1·04 days	IV.	90
Protactinium	Pa ↓	α	$3{\cdot}2 \times 10^4$ years	V.	91
Actinium	Ac ↓	—	13 years	III.	89
Radio-actinium	Rd-Ac ↓	α (β)	18·9 days	IV.	90
Actinium-X	AcX ↓	α	11·2 days	II.	88
Actinon	An ↓	α	3·92 sec.	0.	86
Actinium A	AcA ↓	α	$2{\cdot}0 \times 10^{-3}$ sec.	VI.	84
Actinium B	AcB ↓	(β & γ)	36·1 min.	IV.	82
Actinium C	AcC ↓	α	2·15 min.	V.	83
Actinium C″	AcC″ ↓	β & γ	4·76 min.	III.	81
Pb ex AcC″	Pb	—	—	IV.	82

TABLE V.—THE URANIUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. No.
Uranium I	U_1 ↓	α	$4{\cdot}4 \times 10^9$ years	VI	92
Uranium X_1	UX_1 ↓	β	24·5 days	IV.	90
Uranium X_2	UX_2 ↓	β (γ)	1·14 min.	V.	91
Uranium II	U_{11} ↓	α	$3{\cdot}4 \times 10^5$ years	VI.	92
Ionium	Io ↓	α	$8{\cdot}3 \times 10^4$ years	IV.	90
Radium	Ra ↓	α (β & γ)	1,590 years	II.	88
Radon	Rn ↓	α	3·82 days	0.	86
Radium A.	RaA ↓	α	3·05 mins.	VI.	84
Radium B.	RaB ↓	β (γ)	26·8 mins.	IV.	82
Radium C.	RaC ↓	99·97 per cent. β & γ	19·7 mins.	V.	83
Radium C′	RaC′ ↓	α	10^{-6} sec.	VI.	84
Radium D.	RaD ↓	(β & γ)	22 years	IV.	82
Radium E.	RaE ↓	β	5·0 days	V.	83
Radium F. (Polonium)	RaF Po ↓	α (γ)	140 days	VI.	84
Radium Ω′ (Lead)	RaΩ′ Pb^{206}	—	—	IV.	82
Radium C.	RaC ↓	0·03 per cent. α	—	V.	83
Radium C″	RaC″ ↓	β	1·4 min.	III.	81
Radium Ω″ (Hypothetical)	RaΩ″	—	—	IV.	82

TABLE VI.—THE THORIUM SERIES

Element.	Symbol.	Radiation.	Half-life Period.	Group in Periodic System.	Atc. No.
Thorium . .	Th	α	$1\cdot3 \times 10^{10}$ years	IV.	90
Mesothorium I .	$MsTh_1$	—	6·7 years	II.	88
Mesothorium II .	$MsTh_2$	β & γ	6·13 hours	III.	89
Radiothorium .	RaTh	α (β)	1·90 years	IV.	90
Thorium X .	ThX	α	3·64 days	II.	88
Thoron . .	Tn	α	54·5 sec.	0.	86
Thorium A .	ThA	α	0·14 sec.	VI.	84
Thorium B .	ThB	β & γ	10·6 hours	IV.	82
Thorium C .	ThC	65 per cent. β	1 hour	V.	83
Thorium C′ .	ThC′	α	*ca* 10^{-11} sec.	VI.	84
Thorium D . (Thorium-lead)	ThD Pb^{208}	—	—	IV.	82
Thorium C .	ThC	35 per cent. α	—	V.	83
Thorium C″ .	ThC″	β & γ	3·1 mins.	III.	81
Thorium Ω″ . (Lead)	Th Ω″ Pb^{208}	—	—	IV.	82

place to the right. Thus, uranium X_1, an element in Group IV., loses a β-particle, and becomes uranium X_2, an element in Group V.

The positions of the various radioactive elements in the Periodic Table are shown in the Tables on p. 81.

Now the α-particle consists of the helium nucleus, and bears two positive charges, whilst the β-particle is an electron. It therefore becomes evident that an element A two places to the left of an element B in the Periodic Table must differ from it in possessing two fewer positive charges. The net positive charge on the nucleus

TABLE VII.—The Uranium Series.

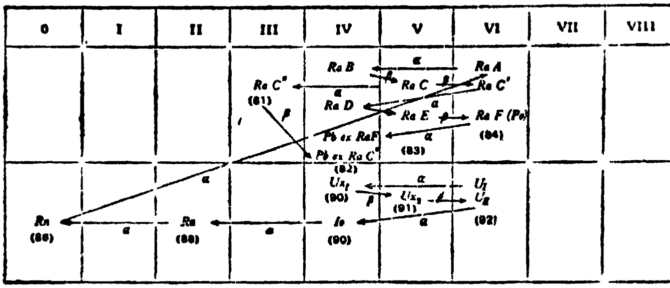


TABLE VIII.—The Thorium Series

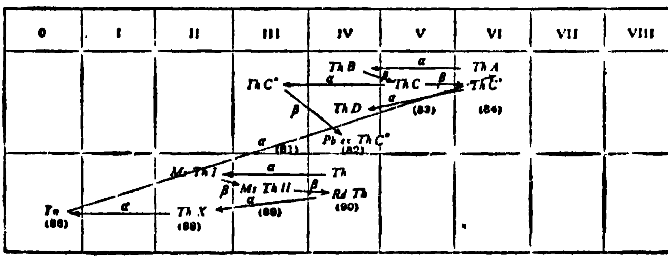


TABLE IX. The Actinium Series.

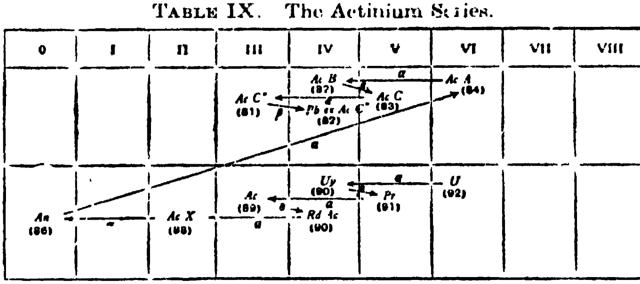


TABLE X.—THE RADIOACTIVE ELEMENTS IN THE PERIODIC TABLE

0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
—	—	—	AcC'''	AcB . ThB	AcC	AcA	—	—
—	—	—	RaC''	RaB . ThD	RaC	RaA	—	—
—	—	—	ThC''	RaD	RaE	RaC'	—	—
—	—	—	—	Pb Ex RaC''	ThC	RaF(Po)	—	—
—	—	—	—	Pb Ex RaF	—	ThA	—	—
—	—	—	—	Pb Ex ThC''	—	ThC'	—	—
—	—	—		Pb Ex AcC''			—	—
			(81)	(82)	(83)	(84)		
An	—	AcX	Ac	UY	UX_2	U	—	—
Rn	—	Ra	$MsTh_2$	RdAc	Pr	UX_1	—	—
Tn	—	$MsTh_1$	—	UX_1	—	—	—	—
—	—	ThX	—	Io	—	—	—	—
—	—	—	—	Th	—	—	—	—
—	—	—	—	Rd Th	—	—	—	—
(86)	—	(88)	(89)	(90)	(91)	(92)	—	—

Atomic numbers in parentheses.

of A is two units less than on that of B. Similarly the element B differs from an element C (formed from it by a β-ray change) in the next place to the right in the Table by possessing one more negative charge on the nucleus, so that when the latter is removed the nucleus increases in charge by 1.

This point is often a troublesome one to grasp. This is not so if it is remembered that it has been shown that both radiations in radioactivity proceed from the nucleus. The β-particle is not an electron removed from the outer sphere of electrons, but one originating in the nucleus. When an unstable nucleus breaks down it does not emit protons and neutrons, the particles which compose it. It seems that under these circumstances the neutron behaves as if it were made up of a proton and an electron, and the electron is emitted. It is this electron which constitutes a β-particle.

The fact that when these radioactive changes take place they are accompanied by simple moves in the positions of the elements in the Periodic Table is very easily explained by supposing that *each element in the Table differs from the one before it by possessing one more net positive charge in the nucleus and one more electron in the extra-nuclear structure.* Indeed, this explanation is demanded by the facts quoted above.

This theory was put forward quite early by van den Broek (1911), but at the time there was very little evidence to support it, and it was not given much attention. When, however, the place changes which take place during radioactive disintegration were discovered in 1913, the theory was a necessary consequence.

At first the theory was applied only to the radioactive elements, no evidence having been gathered to prove its truth in the case of the lighter elements. This was obtained later by Moseley (1913–14), who examined the X-ray spectra of the elements. If the elements are arranged in the order in which they appear in the Periodic Table, allowance being made for the unknown elements, for which gaps are left, and they are then numbered in order, starting with hydrogen as 1, and ending with uranium as 92, the numbers assigned to each element will represent the number of electrons outside the nucleus (called extra-nuclear electrons), and also the resultant positive charge on the nucleus. This number is called the *atomic number* of the element. Moseley was able to determine the atomic numbers of many of the lighter elements. This work will be described in a later section (§ 34).

32. The Nature of Atoms.—We have seen that the nuclear theory of the structure of matter demands that the atom should contain a nucleus, positively charged, the system as a whole being electrically neutral because of the negative electric charges of a cloud of electrons

which surrounds it. The number of these electrons outside the nucleus is the atomic number of the atom. The nucleus itself contains neutrons (§ 30) as well as protons. So long as the resultant charge of the nucleus is positive, and the number of extra-nuclear electrons is sufficient to neutralise this charge, the conditions for the formation of a normal atom are satisfied.

Take, for example, the atom of helium. The mass of any atom is largely accounted for by the nucleus, the electrons being so light as to be negligible when approximate atomic weights are considered. The atomic weight of helium is about 4. This means that there must be four particles with the mass of the proton in the atom. But its atomic number is only 2, and the nucleus has therefore a resultant positive charge of 2 units, and must contain two neutrons. This positive charge is neutralised by the two extra-nuclear electrons. The helium atom can therefore be pictured as in Fig. 32.

Take as a further example the sodium atom. Its atomic number has been found to be 11. It follows that there are 11 electrons outside the nucleus. The atomic weight is 23, so that the atom must contain 23 particles of unit mass, either protons or neutrons. If it is to be electrically neutral, there must be 12 neutrons and 11 protons in the nucleus. The arrangement of the 11 extra-nuclear electrons has been shown, by methods to be outlined in the next chapter, to be in rings containing 2, 8, and 1 electron. The simplified model of this atom is drawn in Fig. 33.

33. The Nature of the Nucleus.—We have already stated that in the nucleus there are protons and neutrons. The arrangement of these particles in the nucleus is even now not correctly known.

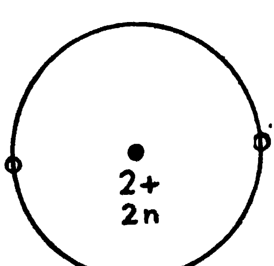


FIG. 32.—The Helium Atom Model (simplified).

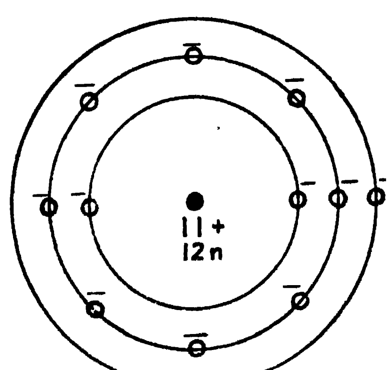


FIG. 33.—The Sodium Atom Model (simplified).

The fact that α-particles are emitted from atoms seems to show that these must be ready made in the nucleus. Exactly how the neutron is to be regarded is a matter of some doubt. It may be thought of for some purposes as a proton and an electron fused together.

It is obvious that the number of protons in the nucleus is equal to the number of extra-nuclear electrons, and therefore to the atomic number, Z. Since the proton has a mass of approximately 1 unit (the normal hydrogen atom contains one proton and one electron, and the mass of the electron is very small compared with that of the proton) and the neutron also has a mass of approximately 1 unit, the masses of all nuclei are approximately whole numbers. This whole number is called the mass number, A. The number of neutrons, N, in the nucleus is clearly equal to $A—Z$.

The forces holding protons and neutrons together in the nucleus are not yet fully understood, but it is known that only certain numbers of these particles can exist together in a stable nucleus. If these numbers are increased artificially by bombardment with neutrons or protons, and their capture by the nucleus, an unstable nucleus is formed, which will later break down to a stable one. However, for a given mass number there are several possible arrangements of protons and neutrons which will give stability. The same is true for a given atomic number, so that altogether over 250 stable nuclei are known, although the number of chemically identifiable elements is less than 100.

Nuclei with the same mass number and different atomic number are called isobares; those with the same atomic number but different mass number are called isotopes. These topics will be more fully dealt with in § 35.

34. Atomic Numbers and their Determination by Moseley's Method.—When an element is bombarded with electrons, X-rays are emitted which are characteristic for the element bombarded. Moseley examined the spectra of the X-rays thus emitted.

The substance under investigation was made the anticathode in a discharge tube. The wavelengths of the X-rays given out were determined by diffraction at a crystal, an X-ray spectrometer similar to that employed by the Braggs in the investigation of crystal structure being used (§ 125). The spectrum was photographed.

The X-ray spectra of the elements are on the whole very simple, consisting of very few lines. In Fig. 34 are shown the spectra of some elements which are adjacent in the Periodic Table. It is seen that the spectra are all alike. They all consist of two lines,[1] one

[1] With the exception of cobalt, for which the spectrum is a little more complicated.

being much stronger than the other. Also, all that is necessary to obtain one spectrum from that of the neighbouring element is to shift it a certain distance to the right or to the left according as whether the one element comes after, or before the other in the Periodic Table.

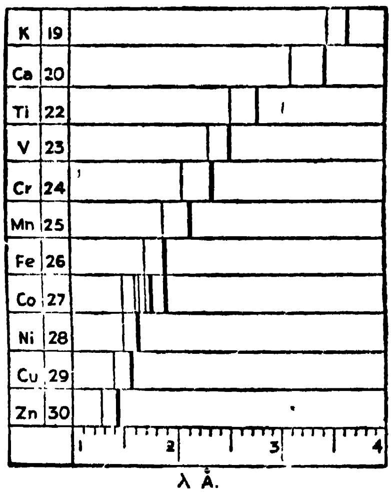


FIG. 34.—*X*-ray Spectra (*K* series).

Three sets of lines were found, which were called the *K*, *L* and *M* lines, the *K* lines being of the shortest wavelength. They are given by all elements. The *L* series is of longer wavelength and has only been found with elements of atomic weight greater than that of neon (*i.e.*, sodium onwards). The *M* radiation, of longer wavelength still, has only been obtained with the very heavy elements. There are four lines in the *K* spectrum, which appear as two sets of two, the lines in each set being very close together, forming what is known as a doublet. An *N* series probably also exists.

Moseley showed that the frequency of a given line in the spectrum was connected with the atomic number of the element by the simple expression

$$\nu = a\,(N - b)^2,$$

where ν is the frequency, N the atomic number, and a and b are constants. For the first line (longest wavelength) of the K spectrum, known as the $K\alpha_1$ line, the constant a is $2{\cdot}47 \times 10^{15}$, and b is 1. This equation is a linear one, and if ν is plotted against N, a straight line should be obtained. That this is the case is shown by the

curves for the three types of spectra (K, L and M) given in Fig. 35.

This work showed the fundamental nature of atomic numbers, and enabled the positive charge on each element to be determined. The work also confirmed the arrangement of the elements in the Periodic Table (pp. 26, 27). It will be remembered that if the elements are arranged in the order of their atomic weights there are several anomalies in the Table. Thus, tellurium comes after iodine, when it is clear from its chemical properties that it should come before. Argon comes after potassium, and since this does not agree with the properties of the elements, they are put out of order in the Table. This alteration was justified by the determination of the atomic numbers of these elements, which indicated that those of tellurium

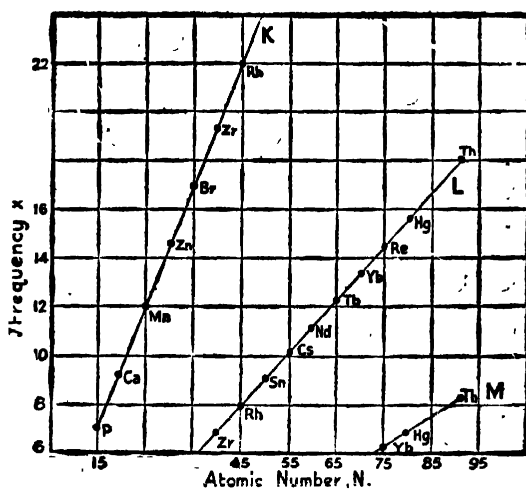


FIG. 35.—Relationship between Frequency of Lines in X-ray Spectra and Atomic Number.

and iodine were 52 and 53 respectively, and of argon and potassium 18 and 19 respectively. The atomic numbers of iron, cobalt and nickel came out to be 26, 27 and 28 respectively, the sequence agreeing with the chemical properties of these elements, but disagreeing with the sequence of their atomic weights. Protactinium and thorium are also now known to be out of order, as far as atomic weight is concerned, but correct with regard to atomic number. The total number of elements from hydrogen to uranium was shown by this work to be 92, and thus the number of rare-earth elements, which could not be satisfactorily defined by the Periodic Table alone, was fixed.

35. Isotopes.—When a radioactive element loses a β-particle its atomic number increases by 1, and so a new element is formed which is one place higher in the periodic system (§ 31). The loss of the β-particle entails, however, practically no loss in mass, as it is so light; so the new element has the same atomic weight as the old. We thus have two elements in the Periodic Table which have the same atomic weight yet differ in atomic number, and in chemical properties. Elements of this type are called *isobares.*

When a radioactive element loses an α-particle, its atomic number is reduced by two and the new element formed occupies a position two places further down the Table (§ 31). If now the new element loses two β-particles successively, the element produced will have the same atomic number as the original one before the series of changes was commenced. The atomic weight, however, will be 4 units less, and so we have two elements occupying the same place in the Periodic Table, yet differing in atomic weight. The chemical properties of such elements are found to be almost exactly the same. Indeed, they are so much alike that it is usually found to be impossible to separate them. Such elements are called *isotopes.*

The atomic number is the number of extra-nuclear electrons, and also the numerical value of the positive charge on the nucleus. It is clear that isotopes possess the same atomic number, and therefore the same number of extra-nuclear electrons, and consequently the same positive nuclear charge. How then do they differ? We have seen previously that the nucleus consists not only of protons, but also of some neutrons. It is in the number of protons and neutrons in the nucleus that isotopes differ. The chemical properties of an atom are known to depend almost entirely on the extra-nuclear electrons, and as these are the same in isotopes the chemical properties of isotopic elements must be almost entirely the same. Except in the case of hydrogen, no chemical difference in isotopes has been found.

It was in connection with the radioactive elements that isotopes were first discovered, but it is now known that they are by no means confined to these elements. Nearly all the elements are now known to be isotopic. When any so-called element is prepared in the laboratory, a pure substance is not obtained, but a mixture of atoms of different atomic weights. The proportions in which these isotopic atoms are present, whenever an element is prepared, are always the same, and so the atomic weight appears to be constant (except in the case of hydrogen, § 40). Thus chlorine consists of two isotopes, of atomic weights 35 and 37. Whenever chlorine is prepared in the laboratory the proportions of these isotopes

present are the same. Hence, whenever the atomic weight of chlorine is determined the same result is obtained.

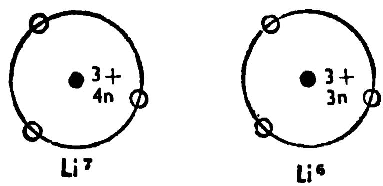


FIG. 36.—Structure of Lithium Isotopes (simplified).

The existence of isotopes can be explained if the possible arrangements of the charges in an atom of an element are considered. To take a simple case, that of lithium, of which the atomic number is 3; there are two isotopes of masses 7 and 6, the former being the predominant one, as can be understood from the fact that the atomic weight of lithium is 6·940. Since the atomic number of both the isotopes of this element is 3, there must be three extra-nuclear electrons. The atomic weight of one of them is 7, hence there must be 7 particles of unit mass in this element. It follows that there must be four neutrons. The atomic weight of the other is 6, and the number of neutrons must be 3. Hence we have two elements with the same atomic number, but with different atomic weights. The properties of the element, being governed by the number of extra-nuclear electrons, are the same in each case, and it would be impossible to distinguish between them chemically. Physically there should be slight differences. For example, the densities of the two forms should be slightly different. It has not been found possible, however, to effect a separation of isotopes on a large scale, with the exception of hydrogen, where the atomic mass of one isotope is double that of the other.

The usual method of denoting any particular isotope symbolically is by placing the mass-number of the isotope to the top right-hand side of the chemical symbol. Thus O^{17} means the isotope of oxygen of mass 17.

Prout's hypothesis, which stated that the atomic weights of all elements were multiples of that of hydrogen, has received striking confirmation from modern work on the structure of matter. We now believe that all elements are made up of protons, neutrons, and electrons, and since hydrogen, the simplest element of all, is made up of one proton and one electron, it is obvious that it is correct to regard all elements as made up on the hydrogen type.

Moreover, the masses of all isotopes are very nearly whole numbers and so here again Prout's hypothesis receives confirmation. It is indeed remarkable that this old hypothesis, which was discredited during last century, should turn out to be true after all, though in a very different way from that thought of by its propounder.

The existence of isotopes of oxygen, of mass 17 and 18, raises the question of the suitability of the oxygen atom as a standard of reference for atomic weights. It has been argued that the oxygen isotope of mass 16 should be taken as standard, but this would make direct comparison, by the usual methods of determining atomic weights, impossible. The proportion of the O^{17} isotope in the ordinary mixture is very small. It has been shown that the ratio of atomic weights calculated on the basis $O = 16$ to those calculated on $O^{16} = 16$ is only 1·00027 to 1. Actually the standard $O = 16$ is used for chemical determinations, and $O^{16} = 16$ in the physical methods (§ 38).

The preparation of almost pure ^{35}Cl by the method of thermal diffusion (§ 39) has led to the suggestion that when the pure isotope is obtained it should be used instead of oxygen to determine the conversion factors for chemical and physical atomic weight scales.

36. The Detection of Isotopes.—Positive-ray Analysis.—The nature and method of production of positive rays have already been briefly mentioned (§ 17). It is by a study of the positive rays emitted from elements that our knowledge of the number of isotopes present in the common elements has been derived.

The first experiments with positive rays which led to important results were made by Sir J. J. Thomson, 1910–12. His apparatus is shown in diagrammatic form in Fig. 37.

The discharge tube A was provided with an aluminium anode D, and the gas under investigation was drawn in through the fine

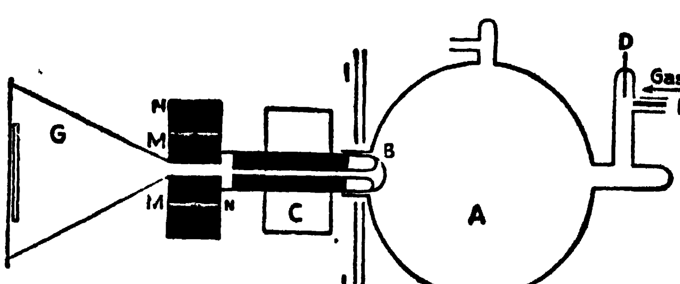


FIG. 37.—Sir J. J. Thomson's Positive Ray Apparatus (diagrammatic).

capillary *E*. The cathode, *B*, again of aluminium, surrounded a brass capillary tube, which was water-cooled by the water-jacket *C*. This tube acted as the perforated cathode, the positive rays passing through it. The positive rays were made to pass through a magnetic field provided by an electromagnet with soft-iron pole pieces *MM*, separated from the former by thin pieces of mica, *NN*. Two soft-iron shields, *II*, prevented the electromagnet from affecting the discharge. An electric field could also be applied. The positive rays after this treatment entered the evacuated vessel *G*, and were recorded on a photographic plate.

The simultaneous action of the electric and magnetic fields caused the positive rays to give rise to parabolas on the photographic plate, and for this reason the method is called Thomson's parabola method. The deviation is dependent upon both the charge and the mass of the particles (§ 16). By comparing the positions of these parabolas on the plate with those due to elements of known atomic weight it was possible to estimate the atomic weight of the element producing them. A line was found due to an element of atomic weight 22. No such element was known. It was at first thought that it was due to carbon dioxide bearing two positive charges (thus giving the effect of an element of mass 22 with one positive charge), but the line did not disappear when the gas was slowly passed through liquid air, whereas that at 44 due to a singly charged carbon dioxide molecule, did disappear. It was also thought that a compound of neon and hydrogen was formed of the composition NeH_2. This would have given the required line, but no evidence of the existence of such a compound outside the tube could be found.

Sir J. J. Thomson considered that he had discovered a new element, and Aston set out to separate the new gas from neon by repeated fractionation with charcoal at the temperature of liquid air, and also by fractional diffusion. After a great deal of work he was able to separate two fractions having molecular weights 20·15 and 20·28 with respect to oxygen as 16 (§ 5). The differences between these two values were too great to account for as experimental error. The two fractions, however, had the same spectra, the same boiling points, and, as far as could be judged, the same chemical properties. Soddy considered that the two elements, of atomic weights 20 and 22, were isotopes, this being the first example of their existence outside the radioactive elements.

Aston now set out to discover more about these elements of mass 20 and 22, and discarded Thomson's parabola method in favour of an arrangement capable of giving more accurate results, called the mass-spectrograph. The arrangement of the apparatus is shown in diagrammatic form in Fig. 38. *B* is the discharge tube, *A* the

anode, and C the cathode which has a slit S_1. A second slit, S_2, is provided to cut down the rays to a fine parallel beam. This passes between the plates J_1J_2 by which the electric field is applied. The beam now passes through a stop-cock L, into the camera part of the apparatus. M is a large electromagnet, by means of which a magnetic field can be applied, at right angles to the electric field. When both fields are applied, the particles are deflected in the plane of the paper by an amount depending upon the ratio e/m. The rays fall on the photographic plate Y, and their positions are measured. The lines obtained are fairly broad, owing to the width of the slit, but the edge is sharp, and this is taken as the position of the line.

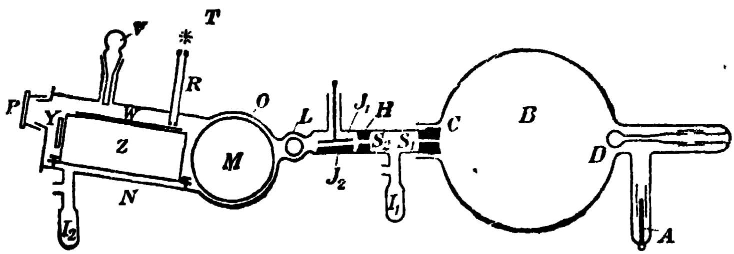


FIG. 38.—Aston's Mass-Spectrograph (diagrammatic). From Aston's "Mass Spectra and Isotopes" (1933), by permission of Messrs. Edward Arnold & Co.

Of course, a standard of measurement is required, and for this oxygen is taken. Lines are obtained at positions corresponding to 32, 16 and 8, due to the molecule, the singly charged atom, and the doubly charged atom of oxygen, respectively. By adding carbon dioxide to the tube, lines are obtained at 6, 12, 28 and 44, being due to C^{++}, C, CO and CO_2 respectively, thus providing a number of standards by which to measure the lines produced by other elements.

When neon was introduced into the tube, lines were obtained at 22, 20, 11 and 10. There could be no further doubt that neon was not a pure element, but made up of two isotopes, of atomic weights 22 and 20. Isotopes of chlorine and argon were also found.

This apparatus was only applicable for gases, and it soon became important to discover whether isotopes of the solid elements also existed. For this purpose Aston devised the method of the "accelerated anode ray," in which the positive rays were produced

by coating the anode with a suitable salt mixture, containing the element to be tested. Positive ions are emitted and are accelerated in their passage to the cathode, and can then be treated as positive rays. In this way the majority of the elements have been examined.

The existence of isotopes can be shown, and their masses determined, by means of a different apparatus, devised by Dempster (*Phys. Rev.*, 1918, **11**, 316) and shown diagrammatically in Fig. 39. In this the positive particles obtained by heating salts on a platinum strip, or by bombarding compounds containing the element under investigation by electrons, are passed through a definite potential difference, and then pass through a slit, S_1, into the analysing chamber where they are acted upon by a strong magnetic field,

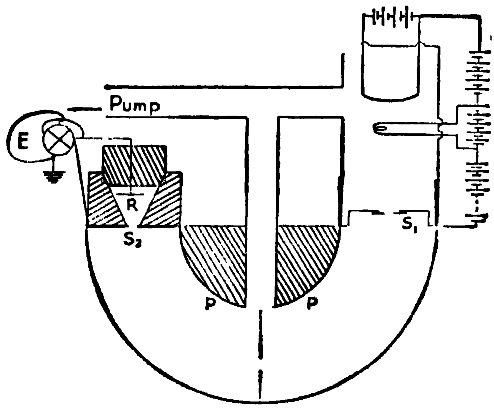


FIG. 39.—Dempster's Positive Ray Apparatus (diagrammatic).

bending them into a semicircle. They then pass through a further slit, S_2, and fall on a plate, R, connected with an electrometer E. The potential required to bring a particle of known mass on to the detecting electrometer is measured. Actually, the potential is varied, the magnetic field being kept constant, and the ionic current produced in the electrometer is measured. This shows peaks when the particles fall on the plate, the maxima corresponding to particles of definite masses, which can be obtained after standardising the instrument.

Almost all elements have been shown to have isotopes. Even hydrogen itself has been shown to have an isotope of mass 2 (§ 40). The Table below (Table XI.) gives a list of the isotopes discovered up to 1940.

TABLE XI.—TABLE OF ISOTOPES

The isotopes are given in the order of their abundance in the elements. Radioactive isotopes produced artificially are not included in this list.

Atomic No.	Element.	Atomic Wt.	Isotopes.
1	Hydrogen .	1·0081	1, 2, 3
2	Helium . .	4·003	4, 3
3	Lithium .	6·940	7, 6
4	Beryllium .	9·02	9
5	Boron . .	10·82	11, 10
6	Carbon . .	12·010	12, 13
7	Nitrogen .	14·008	14, 15
8	Oxygen .	16·000	16, 18, 17
9	Fluorine .	19·00	19
10	Neon . .	20·183	20, 22, 21
11	Sodium . .	22·997	23
12	Magnesium .	24·32	24, 25, 26
13	Aluminium .	26·97	27
14	Silicon . .	28·06	28, 29, 30
15	Phosphorus .	31·02	31
16	Sulphur. .	32·066	32, 34, 33
17	Chlorine .	35·457	35, 37
18	Argon . .	39·944	40, 36, 38
19	Potassium .	39·096	39, 41, 40
20	Calcium. .	40·08	40, 44, 42, 48, 43, 46
21	Scandium .	45·10	45
22	Titanium .	47·90	48, 46, 47, 49, 50
23	Vanadium .	50·95	51
24	Chromium .	52·01	52, 53, 50, 54
25	Manganese .	54·93	55
26	Iron . .	55·84	56, 54, 57, 58
27	Cobalt . .	58·94	59, 57
28	Nickel . .	58·69	58, 60, 62, 61, 64
29	Copper . .	63·54	63, 65
30	Zinc . .	65·38	64, 66, 68, 67, 70
31	Gallium. .	69·72	69, 71
32	Germanium .	72·60	74, 72, 70, 73, 76
33	Arsenic . .	74·91	75
34	Selenium .	78·96	80, 78, 76, 82, 77, 74
35	Bromine .	79·916	79, 81
36	Krypton .	83·7	84, 86, 82, 83, 80, 78

Atomic No.	Element.	Atomic Wt.	Isotopes.
37	Rubidium .	85·48	85, 87
38	Strontium .	87·63	88, 86, 87, 84
39	Yttrium .	88·92	89
40	Zirconium .	91·22	90, 92, 94, 91, 96
41	Niobium .	93·3	93
42	Molybdenum .	95·95	98, 96, 95, 92, 94, 100, 97
43	Masurium .	?	
44	Ruthenium .	101·7	102, 101, 104, 100, 99, 96, (98)
45	Rhodium .	102·91	103, 101
46	Palladium .	106·7	106, 108, 105, 110, 104, 102
47	Silver . .	107·880	107, 109
48	Cadmium .	112·41	114, 112, 111, 110, 113, 116, 106, 108, 118
49	Indium . .	114·76	115, 113
50	Tin . .	118·70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
51	Antimony .	121·76	121, 123
52	Tellurium .	127·61	130, 128, 126, 125, 124, 122, 123, (120)
53	Iodine . .	126·92	127
54	Xenon. .	131·3	132, 129, 131, 134, 136, 130, 128, 124, 126
55	Cæsium .	132·91	133
56	Barium . .	137·36	138, 137, 136, 135, 134, 130, 132
57	Lanthanum .	138·92	139
58	Cerium . .	140·13	140, 142, (136, 138)
59	Praseodymium	140·92	141
60	Neodymium .	144·27	142, 144, 146. 143, 145, 148, 150
61	Illinium. .	?	
62	Samarium .	150·34	152, 154, 147, 149, 148, 150, 144
63	Europium .	152·0	153, 151
64	Gadolinium .	156·9	156, 158, 155, 157, 160, 154, 152
65	Terbium .	159·2	159
66	Dysprosium .	162·46	164, 162, 163, 161, 160, 158
67	Holmium .	163·5	165
68	Erbium .	167·2	166, 168, 167, 170, 164, 162
69	Thulium .	169·4	169

Atomic No.	Element.	Atomic Wt.	Isotopes.
70	Ytterbium .	173·04	174, 172, 173, 176, 171, 170, 168
71	Lutecium .	175·0	175
72	Hafnium .	178·6	180, 178, 177, 179, 176, 174, (172)
73	Tantalum .	180·88	181
74	Tungsten .	183·92	184, 186, 182, 183, 180
75	Rhenium .	186·31	187, 185
76	Osmium .	190·2	192, 190, 189, 188, 187, 186, 184
77	Iridium .	193·1	193, 191
78	Platinum .	195·23	195, 194, 196, 198, 192
79	Gold . .	197·2	197
80	Mercury .	200·61	202, 200, 199, 201, 198, 204, 196

Atomic No.	Element,	Atomic Wt.	Isotopes	Radioactive Isotopes.
81	Thallium .	204·39	205, 203	207, 208, 210
82	Lead . .	207·21	208, 206, 207, 204 (203, 205, 209)	210, 211, 212, 214
83	Bismuth .	209·00	209	210, 211, 212, 214
84	Polonium .	210·00		210, 211, 212, 214, 215, 216, 218
85	—	—	—	—
86	Emanation (Radon). .	222		222, 219, 220
87	Eka-cæsium .	?		
88	Radium. .	226·05		226, 223, 224, 228
89	Actinium .	?		227, 228
90	Thorium .	232·12	232	232, 227, 228, 230, 234
91	Proto-actinium	?		231, 234
92	Uranium .	238·07		238, 235, 234

37. The Whole-Number Rule, and Deviations from it.—Attention has already been called to the fact that the masses of isotopes are all very nearly whole numbers, and that therefore Prout's hypothesis is more nearly true than was believed during the last century. This fact, of course, is what would be expected when it is realised that the electron has an extremely small mass, and that even 92 of them, the maximum number of extra-nuclear electrons found in any element occurring naturally, will weigh only a small fraction of a unit.

It is, however, true that there is sometimes a very slight deviation from this rule that the mass of any isotope is a whole number. Hydrogen itself has an isotope of mass 1·008 on the standard that the mass of the oxygen atom is 16. This is explained on the modern view that mass is entirely electrical in origin. If two charges are brought close to each other, it can be shown that the interaction of their fields causes a loss in mass. This effect is only found when the separation of the two charges is very small indeed. The total mass of the nucleus will not be the sum of the masses

TABLE XII.—PACKING-FRACTIONS OF ATOMS

Atom.	Packing-fraction. $\times 10^4$.	Atom.	Packing-fraction $\times 10^4$.
H . .	$77 \cdot 8 \pm 1 \cdot 5$	As . .	$-8 \cdot 8 \pm 1 \cdot 5$
He . .	$5 \cdot 4 \pm 1$	Cr^{52} . .	-10 ± 3
Li^{6} . .	$20 \cdot 0 \pm 3$	Kr^{78} . .	$-9 \cdot 4 \pm 2$
Li^{7} . .	$17 \cdot 0 \pm 3$	Br^{79} . .	$-9 \cdot 0 \pm 1 \cdot 5$
B^{10} . .	$13 \cdot 5 \pm 1 \cdot 5$	Kr^{80} . .	$-9 \cdot 1 \pm 2$
B^{11} . .	$10 \cdot 0 \pm 1 \cdot 5$	Br^{81} . .	$-8 \cdot 6 \pm 1 \cdot 5$
C . .	$3 \cdot 0 \pm 1$	Kr^{82} . .	$-8 \cdot 8 \pm 1 \cdot 5$
N . .	$5 \cdot 7 \pm 2$	Kr^{83} . .	$-8 \cdot 7 \pm 1 \cdot 5$
O . .	$0 \cdot 0$	Kr^{84} . .	$-8 \cdot 5 \pm 1 \cdot 5$
F . .	$0 \cdot 0 \pm 1$	Kr^{86} . .	$-8 \cdot 2 \pm 1 \cdot 5$
Ne^{20} . .	$0 \cdot 2 \pm 1$	Mo^{98} . .	*ca* $-5 \cdot 5$
Ne^{22} . .	*ca* $2 \cdot 2$	Mo^{100} . .	*ca* $-5 \cdot 5$
P . .	$-5 \cdot 6 \pm 1 \cdot 5$	I . .	$-5 \cdot 3 \pm 2$
Cl^{35} . .	$-4 \cdot 8 \pm 1 \cdot 5$	Sn^{120} . .	$-7 \cdot 3 \pm 2$
A^{36} . .	$-6 \cdot 6 \pm 1 \cdot 5$	Cs . .	-5 ± 2
		Xe^{134} . .	$-5 \cdot 3 \pm 2$
Cl^{37} . .	$-5 \cdot 0 \pm 1 \cdot 5$	Ba . .	$-6 \cdot 1$
		Hg^{200} . .	$+0 \cdot 8 \pm 2$
A^{40} . .	$-7 \cdot 2 \pm 1$	Tl . .	$+1 \cdot 8$
		Pb^{206} . .	$+0 \cdot 8 \pm 2$

of the protons and neutrons, but slightly less than this. This, of course, will also make itself felt in the total mass of the atom, which is made up of the mass of the nucleus and of the extra-nuclear electrons. In the hydrogen atom there is only one proton in the nucleus, and so there will be none of this effect. Its mass will therefore be slightly greater than one-sixteenth of the mass of the oxygen atom. This effect is called close-packing. The loss of mass obviously depends upon the closeness of the packing of the charges in the nucleus.

The packing of particles in the nuclei of all elements is not the same, and so the elements show slight deviations from the whole number rule due to the packing effect. Aston, with a more refined mass-spectrograph, has been able to determine the "packing-fraction" or divergence from the whole number rule, for several atoms, and the results are shown in Table XII.

The packing-fraction obviously measures the forces which keep the constituents of the nucleus bound together. If the value is high the neutrons are further separated from the protons, and the atom is therefore less stable. If the value is low the nucleus will be more stable. A curious alternation is noted in the packing-fraction as we proceed from elements of odd atomic number to those of even atomic number. There are several other properties which alternate in the same way.

As mass and energy are interconvertible, the packing-fraction is of considerable importance in connection with the utilisation of atomic energy (§ 43c).

38. The Physical Determination of Atomic Weights.—If we knew the packing-fractions of the different elements and the proportions of the isotopes occurring in the element as commonly prepared, it would be possible to calculate the atomic weight.

This had been attempted almost as soon as the existence of isotopes of the common elements had been proved. The relative abundance of the isotopes was estimated visually from the photographs obtained by the first mass-spectrograph. At first the results were found to be in excellent agreement with the chemical values; but when krypton was studied, the first serious discrepancy arose. With this element six lines were found, each of them corresponding to an integral mass, and therefore belonging to a definite isotope. The position of the centre of gravity of this group was estimated, and gave an atomic weight for the element of 83·5 $\pm$ 0·3. The international figure, based on determinations of the density, was 82·92. With boron, two isotopes were found of masses 10 and 11, and the atomic weight calculated from these was less than the chemical value of 10·90. Xenon gave a mean value of 131·3 $\pm$ 0·3, whereas the international value

was 130·2. The greatest discrepancy of all was with antimony, the isotopes of which were 121 and 123, whereas the international atomic weight was lower than either, viz., 120·2. Beryllium, according to positive ray analysis was a simple element, and hence its atomic weight should be integral. The value accepted was 9·1, which was considered to be too far removed from an integer. The fact that the physical values differed from the chemical in these cases led to a redetermination of these atomic weights by chemical methods, and in the cases of boron, beryllium and antimony, the discrepancies were reduced to very small magnitudes, although they remained for krypton and xenon.

The first actual determinations of the relative abundance of isotopes in a given element, apart from the somewhat rough visual determination, were carried out by Dempster, who analysed the positive rays magnetically, and compared the currents caused by the rays due to the various isotopes, when they ionised a gas. The method has already been described (§ 36). The masses of the isotopes were not determined, but by assuming that the whole number rule was valid, he was able to show that the atomic weights of potassium, magnesium, calcium and zinc were in fair agreement with those derived chemically.

In 1925, Aston devised the second mass-spectrograph, which has already been described, and with its aid he was able to show that the whole number rule was not strictly valid owing to the existence of "packing-fractions."

When these are known the correct mass of any isotope can be written down, and this is, of course, a preliminary to any calculation of atomic weights by the physical method. It was still necessary, however, to devise some more accurate method of comparing the relative abundance of the isotopes in any given element, and this was done by Aston, who invented a photometric method of estimating the intensity of the blackening on the photographic plate upon which the isotopic lines were registered.

As this work is of extreme importance as providing very accurate values for the atomic weights of elements, it will be described fairly thoroughly. At first krypton was taken as the standard element, as it has six isotopes, and provides rays in which it is safe to assume that the proportion of the isotopes does not vary. The relative abundance of the isotopes of mass 84 and 86 respectively was first determined by the method of intermittent exposures. By a special mechanical arrangement the lines were photographed with normal and with reduced times of exposure, the two images being separated from each other by slightly varying the electric field. The effect of this change of field was eliminated by taking the next picture with

the field change reversed. By breaking up the exposure into small ones the continuous change in the intensity of the source was compensated for as far as possible. The ratio of the exposures was altered until the stronger of the two lines and the normal one of the weaker were virtually equal. The ratio for correct equality was calculated, and when corrected for the effect of the penumbra of the neighbouring lines and for the relative positions of the two lines on the plate, the value 3·41 was obtained for the ratio of the abundance of Kr^{84} compared with that of Kr^{86}. The process was repeated for the other isotopes, and the following figures were obtained for the percentage abundance of the isotopes :—

78	80	82	83	84	86
0·42	2·45	11·79	11·79	56·85	16·70

These give a " mean mass number " of 83·857, which, when corrected, for a packing-fraction of − 8·8 in 10,000 gives the atomic weight (O = 16) as 83·783. This was considerably higher than the chemical value (82·92) then accepted. Allen and Moore (*J. Amer. Chem. Soc.*,

TABLE XIII.—CHEMICAL AND PHYSICAL ATOMIC WEIGHTS

Element.	Atomic Number.	International Atomic Weight.	Physical Atomic Weight.	Element.	Atomic Number.	International Atomic Weight.	Physical Atomic Weight.
H	1	1·0078	1·00761	Sr	38	87·63	87·64
He	2	4·002	4·00136	Nb	41	93·3	92·90
Li	3	6·940	6·928	Mo	42	96·0	95·97
B	5	10·82	10·803	Ru	44	101·7	(101·1)
C	6	12·00	12·0037	Sn	50	118·70	118·71
N	7	14·008	14·008	Sb	51	121·76	121·78
O	8	16·000	16·000	Te	52	127·61	127·58
F	9	19·00	18·996	I	53	126·932	126·91
P	15	31·02	30·98	Xe	54	131·3	131·26
Sc	21	45·10	44·96	Cs	55	132·91	132·91
Cr	24	52·01	52·01	Ba	56	137·36	137·43
Zn	30	65·38	65·33	Ta	73	181·4	180·89
Ge	32	72·60	72·65	W	74	184·0	183·96
As	33	74·91	74·92	Re	75	186·31	186·22
Se	34	78·96	78·96	Os	76	191·5	190·31
Br	35	79·916	79·911	Hg	80	200·61	200·62
Kr	36	83·7	83·767	Tl	81	204·39	204·41
Rb	37	85·44	85·43	Pb	82	207·22	207·19

(From the *Journal of the Chemical Society*, 1932, 2893 ; with some corrections from more recent work.)

1931, **53**, 2512) then redetermined the density of krypton from liquid air residues, and found the value 83·6 for the atomic weight, which is in agreement with Aston's figure. The international value now accepted is 83·7.

The atomic weights of the other elements were more difficult to determine, as the apparatus would not resolve the lines sufficiently to enable one of the lines to be photographed between two others without overlapping. In this case, a large number of short exposures of different times was used, and the best mean values adopted from the curves obtained.

The atomic weights of a large number of elements have now been determined by this physical method, and the results are given in Table XIII.

Where the values differed from those accepted and determined on the chemical basis, re-determination on this basis has usually shown that the physical method gave the correct result. The atomic weight of selenium, which differed from the chemical value by 0·24 unit, was re-determined chemically by Hönigschmid, who found a value close to that obtained physically.

There are many difficulties yet to be overcome in the photometry of the mass-spectrograph, but there is no doubt that it is capable of providing results at least equal to those derived chemically, and it is exceedingly interesting to find that the results of the two methods, so different in principle, are so near to each other. This indicates quite clearly that the theories on which both are based are essentially correct.

39. The Separation of Isotopes.—The separation of isotopes is a matter of extraordinary difficulty. It is clear that as there are no differences in chemical properties (except in the case of hydrogen, where compounds of the two isotopes separately are found to enter into certain reactions at different rates), the only methods of separation that can be used must involve some physical property.

The method that strikes one as being immediately applicable is that of diffusion. If there are differences in the density, it should be possible to separate the isotopes by the process of diffusion. This has been tried with hydrogen chloride, but the process is very tedious, since the difference in density is so small. Harkins, who attempted to separate hydrogen chloride into two fractions, employed 20,000 litres of the gas, and obtained finally a difference of molecular weight of 0·055 unit.

Aston, somewhat earlier, had attempted to separate neon into fractions by the same method, and finally obtained two fractions having densities 20·15 and 20·28 respectively, the normal density

being 20·20. The neon isotope of mass 22 has now been separated perfectly from the isotope of mass 20 by a diffusion process.

The fact that the rate of evaporation of a mixture of atoms varies with the mass of the atom has also been used for their separation. A greater number of the light atoms will escape from the surface in a given time, and the residue will therefore be richer in the heavier atoms. The rates of evaporation of otherwise identical atoms under the same conditions are inversely proportional to the square root of their masses. By keeping the pressure on the surface of the liquid low, none of the atoms escaping will return to the surface, and so a partial separation can be effected.

The method has been used by Brönsted and Hevesy in the separation of mercury into two fractions, one containing a greater proportion of the lighter isotopes, and one containing a greater proportion of the heavier. The mercury was allowed to evaporate in a high vacuum, at a temperature of 40°–60° C., and was condensed on a surface 1–2 cm. away, cooled in liquid air. Actually, the mercury was placed in the space between the two walls of a Dewar flask containing liquid air. The lighter atoms which evaporated off first were condensed to the solid state on the cold surface, and therefore had no chance of returning to the liquid. After the evaporation had gone on for some time, the mercury residue was removed, and the solid distillate was melted, and kept apart. The process was repeated with this, and so on. If the density of ordinary mercury is taken as 1, the densities of the lightest and heaviest fractions were 0·99974 and 1·00023 respectively.

Harkins improved the apparatus, and by working on a larger scale was able to obtain mercury having an atomic weight differing by 0·189 unit from that of ordinary mercury. The experiment has also been repeated by Hönigschmid and Birckenbach, who obtained fractions of atomic weights 200·564 and 200·632 respectively, whereas the atomic weight of ordinary mercury is 200·61.

The method has also been applied to potassium by Hevesy, and to zinc by Egerton.

The fractionation of isotopes by electrolysis is a method that has been used, particularly in the separation of the hydrogen isotopes. Kendall (1933) claims to have effected a slight separation of mercury isotopes by this method. Electrolysis of an acid solution of mercurous nitrate, using a low voltage, and low current density, gave mercury with a density 0·999981 that of ordinary mercury.

The method of thermal diffusion has been applied very success-

fully to the separation of isotopes by Clusius and Dickel (1938). It is based primarily on an observation by Enskog (1911), who showed that if a gaseous mixture of molecules of different mass was enclosed in a tube which was hotter at one end than at the other, the heavier molecules would tend to diffuse towards the cooler end. This process of thermal diffusion would go on until it was balanced by the effect of ordinary diffusion, which would, of course, work in the opposite direction.

Whilst this process may bring about a reasonable separation of gases which differ considerably in mass and nature, without modification it is of very little use for the separation of isotopes which do not differ much in mass. In the method devised by Enskog, and used by Chapman and Dootson for the separation of a mixture of hydrogen and carbon dioxide, convection currents are avoided by having the hot plate parallel to, and above, the cold one. If, however, the parallel plates are placed vertically convection currents may be made to enhance the separation. In the diagram convection currents occur as shown by the arrows. At the same time thermal diffusion brings about a concentration gradient with the lighter component near the hot plate. This gas reaching A is carried upwards, that at B travels downwards. This means that the lighter fraction will become concentrated at the top of the apparatus and the heavier at the bottom. In the apparatus used by Clusius and Dickel for this purpose, a vertical glass tube was used with an electrically heated wire running down the centre. The glass tube was cooled on the outside by a current of cold water. With apparatus of this kind, the tube being 36 metres long, the isotopes of chlorine have been separated almost completely.

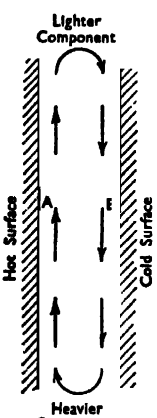


FIG. 39a.

The method has been used to obtain the uranium isotope of mass 235 for nuclear chain reactions in uranium (§ 43b). In this case uranium hexafluoride, UF_6, was used as the carrier gas.

The method of thermal diffusion can also be applied to liquids, but is limited to substances which are not decomposed at the temperature of the hot wire.

40. The Hydrogen Isotope, H^2.—One of the most outstanding pieces of recent research has been the discovery of the hydrogen isotope of mass 2. The fact that the physical atomic weight of hydrogen differed from the chemical value, though by very little (the physical atomic weight is 1·00756, whilst the chemical value is

1·0078, both calculated on the chemical standard) led Birge and Menzel (*Phys. Rev.*, 1931, **37**, 1669) to suggest that ordinary hydrogen consists of a mixture of the atoms of mass 1 (approx.), and a very small amount of an isotope of double this mass, only the former having been observed in Aston's experiments fixing the physical atomic weight. The more recent work has shown that the difference between the two atomic weights can be approximately accounted for by the proportion of the isotope present, the ratio of the abundance of H^1 to that of H^2 being 6,500 to 1.

The residues left after the evaporation of large quantities of liquid hydrogen were found to give faint lines corresponding to H^2, when examined spectroscopically [Urey, Brickwedde and Murphy (*Phys. Rev.*, 1932, **40**, 1)]. Bainbridge (*Phys. Rev.*, 1932, **41**, 115) has also demonstrated the existence of the isotope by means of the mass-spectrograph, obtaining a value for its mass of $2{\cdot}01351 \pm 0{\cdot}00018$, referred to $O^{16} = 16$. The nucleus of the new isotope might consist of two protons and one electron, but with the discovery of the neutron and the positive electron, alternative structures for this nucleus (which has been called the deuteron), can be devised. It may consist of two neutrons and one positive electron (§ 43d).

The separation of the hydrogen isotope was carried out by Washburn and Urey, in 1932, by the examination of water from commercial electrolytic cells which had been working for some years. There was shown to be more H^2 in this water than in ordinary water. Lewis and Macdonald electrolysed 20 litres of water from an old electrolytic cell, which contained alkali, with a current of 250 ampères, until the volume was only 10 per cent. of the original. One-tenth was neutralised with carbon dioxide and the rest distilled. Then the two sets were combined. The process was repeated until only $\frac{1}{2}$ c.c. was left. The water they finally prepared had a specific gravity of 1·073, and probably contained 65 per cent. of heavy water, H^2_2O.

If water is distilled through a long fractionating column, quite a large separation of isotopes results, especially if the work is carried out under reduced pressure. Practically pure "heavy water" was obtained by Lewis and Macdonald, who found that its freezing point was + 3·8° C., and boiling point 101·42° C. Many other physical properties of the water have been examined. It has a maximum density at 11·6° C.

The hydrogen isotope, H^2, itself has been prepared in a state of purity by Hertz, Schutze, and Harmsen, by a process of diffusion. Since the two isotopes differ in mass by approximately 100 per cent., their separation by this method should be much more easy than for other elements. Water from an electrolysis apparatus was reduced

by magnesium. The hydrogen thus obtained consisted of H_2^1, and composite molecules, made up of an atom of each isotope, H^1H^2, with only a small amount of H^2. By passing the electric discharge through the mixture, the composite molecules were broken down into their atoms, which recombined to form molecules of H_2^1 and H_2^2. The mixture now contained only the two molecular species, and was readily separated into the two constituents by diffusion. In this way the H^2 isotope was obtained spectroscopically pure.

In most cases, the chemical properties of isotopes are very nearly the same, and this also applies to compounds made from different isotopes. In the case of hydrogen, however, this does not appear to be so, for the compounds made from one isotope are different in some important respects from those made from the other. Thus, "heavy water," which is H_2^2O, is toxic to certain forms of life, a fact which had been predicted by Lewis even before the water was obtained.

Heavy hydrogen probably reacts more slowly than the lighter form. It has been reported that electrolytic hydrogen is more active in the Haber ammonia synthesis than other hydrogen prepared from steam. In fact, the velocity of reaction is 10–40 per cent. greater. This is probably due to the fact, that when water is electrolysed, the heavy isotope is left in the water in the cell, whilst the lighter one is evolved.

It is a matter of some importance to note what effect the discovery of this isotope will have on the determination of the composition of substances containing hydrogen. In determining the composition of water, or of ammonia, or any other gas containing hydrogen, it will now be necessary to make certain that the "pure" gas is used, or else its composition must be known. The source of the hydrogen used in the experiments must be stated. This difference in composition of hydrogen obtained from different sources explains the differences that have been found in the composition of water (§ 13).

It is clearly advantageous to retain the oxygen standard for atomic weight determinations in the light of the new discovery. As has been stated already (§ 11), the determination of the atomic weights of solid elements usually involves the determination of the equivalents. This is often found by determining the weight of the element that will combine with 8 gms. of oxygen. If, however, the scale H = 1 is taken, the equivalent of oxygen is no longer 8, and moreover its determination will not be a simple matter, since it depends on the composition of water.

It has been pointed out that, with the existence of the two isotopes of carbon, C^{12} and C^{13}, and the two isotopes of hydrogen, the properties of which are different from each other, a new organic

chemistry might be possible, in which the compounds were made by combination of the various pure isotopes. The use of heavy water in medicine may also prove a useful field of research. A preparation containing 30 per cent. H_2^2O is now a commercial article.

Heavy water has proved to be of great importance in the controlled chain-fission of uranium (§ 43b).

41. Variation of the Atomic Weight of an Element with its Source.—It is a curious fact that no matter how an element is prepared chemically in the laboratory, the proportion of the isotopes present in it is always the same. This may not be so, however, with naturally occurring elements and compounds. Some of these may have been formed from radioactive sources, and may have different atomic weights according to the source from which they are derived. This is known to be the case with lead. Lead minerals derived from different radioactive sources have different atomic weights. Thus the atomic weight of lead from a deposit supposed to have come from uranium was 206.08, a mixed Australian mineral gave an atomic weight 206·34, whilst ordinary lead has the atomic weight 207·19.

The atomic weight of calcium is found to differ according to its source. A. V. Frost and O. Frost claim to have found a concentration of Ca^{44} in a specimen of potash felspar, the value 40·23 being obtained for the atomic weight of the calcium in this mineral, whereas that of ordinary calcium is 40·08.[1]

The atomic weight of three specimens of boron from different sources gave the values 10·847, 10·823 and 10·818. The differences are too great to be ascribed to experimental error. As boron is light, its isotopes differ in mass by 10 per cent., and consequently the effect is more marked with this element than with others.

The variation in atomic weight of hydrogen according to its source has already been mentioned (§ 40).

42. Atomic Transmutation.—The radioactive elements are continually undergoing spontaneous disintegration, and new elements are being formed. This process is going on every day, and no method is known of stopping, or of accelerating it. Thus, transmutation is occurring, but we have no control over it.

It is to the transmutation of ordinary elements that attention is called by recent research. The properties of an element depend on the atomic number, which is numerically identical with the resultant positive charge on the nucleus. To transmute an element, the nucleus must be altered artificially, *i.e.*, the process which goes on naturally with the radioactive elements must be carried out in the

[1] The Ca of atomic weight 40·23 is supposed to have been formed from K^{41} by a β-ray change. The existence of Ca of high atomic weight in minerals has been confirmed by Kendall, Smith, and Tait, *Nature*, 1933, **131**, 688.

laboratory. Practically all the mass of the atom is concentrated in the nucleus, and consequently almost all the energy. If any change is to be brought about in the nucleus, energy of a similar amount and concentration must be supplied.

α-particles from radioactive bodies are fairly heavy, and although their speeds do not approach those of β-particles, they are possessed of a fairly great amount of energy. According to the Einstein theory of relativity, the mass of a moving charged body depends upon its velocity, becoming infinite when the velocity is that of light (§ 22). The more rapidly the α-particle moves the greater is its kinetic energy ($\frac{1}{2}mv^2$, where m is the mass, and v the velocity), not only because the velocity increases, but because, in consequence of the latter, the mass is also increased. The more rapidly moving α-particles will therefore be possessed of high energy.

Rutherford, in 1919, found that when α-particles from a radioactive source were fired into nitrogen, a certain amount of transmutation took place. The tracks of the particles were made evident by means of the Wilson cloud-chamber (§ 21), and evidence was found of the formation of high-speed hydrogen nuclei or protons. It must be remembered that the amount of transmutation was exceedingly small, and would never have been observed unless extraordinarily sensitive methods had been used for detecting it. Other elements were found to be disintegrated in the same way. Boron, nitrogen, fluorine, sodium, aluminium, phosphorus, neon, magnesium, silicon, sulphur, argon and potassium, all gave a small number of charged hydrogen nuclei on bombardment with swift α-particles.

It has been pointed out that in order to obtain transmutation, particles possessing high energy are required. These need not be α-particles; protons will also serve the purpose. Attempts to use protons, however, from sources such as discharge tubes, were not at first successful, owing to the fact that it seemed to be necessary to employ very high potentials in the discharge tubes to obtain protons with the requisite energy. These difficulties were entirely overcome by the adoption of a device for enhancing the energy of the protons. As early as 1902, Wien had shown that protons could be accelerated as they passed through the perforated cathode. After passing through the "canal," they were passed into a highly evacuated space, and then accelerated by means of an electric field of great intensity.

This method of obtaining rapid protons has been used with success by Cockcroft and Walton. By passing the protons from a discharge tube through a field of 125,000 volts in an evacuated space they were speeded up to such an extent that they possessed velocities com-

parable with those of the α-particles from polonium. Bombardment with these high-speed protons was applied to the disintegration of lithium. A large number of α-particles was emitted. The change appears to be that the nucleus of lithium, of mass 7, and atomic number 3, which contains 3 protons and 4 neutrons, takes up one proton, and then splits into two α-particles of mass 4 and charge 2 :—

$$Li^7 + H^1 = He^4 + He^4.$$

Boron is quite easily broken down by protons, with the emission of α-particles. The boron nucleus of mass 11, and containing five protons, takes up a proton of mass 1, and breaks down into three α-particles :—

$$B^{11} + H^1 = 3He^4.$$

Another method of producing rapid protons for these experiments has been devised by Lawrence in America, and by Gerthsen in Germany. They have accelerated the particles by making them pass through the same potential over and over again. The process is known as " multiple acceleration," and is carried out in a cyclotron. In this way they have been able to produce protons of energy 1·5 million volts, by using an accelerating potential of only 10,000 volts. Oliphant and Rutherford have devised a special accelerating tube which will produce a narrow and intense stream of protons with voltages up to 200 kilovolts.

Other types of apparatus used for the production of high-speed particles are the betatron and the synchroton.

Hard γ-rays are also possessed of sufficient energy to bring about disintegration. It will be shown in the next chapter that the energy associated with a radiation of frequency ν, is proportional to the frequency, Thus, the smaller the wavelength, the greater the frequency, and the greater the energy.

Neutrons are particularly valuable as bombarding particles for bringing about atomic transmutation because they are uncharged. They can therefore penetrate atoms with a much smaller chance of capture. Charged particles are slowed down considerably in passing through matter because of the other charged particles (electrons and protons) with which they interact. A neutron, however, goes straight on until it encounters a nucleus head-on; if it is then captured an unstable nucleus may result, when an artificially radioactive nucleus will have been formed. On the other hand if the nucleus is stable, the original element will have been changed to another.

Experiments on atomic transmutation have been carried out, using the nucleus of the hydrogen isotope, H^2, or deuteron, as the

firing particle. It is possible in this way to transform lithium into helium, and nitrogen into carbon.

$$Li^6 + H^2 = 2He^4,$$
$$N^{14} + H^2 = C^{12} + He^4.$$

Kirchner has used helium as a firing particle, and has obtained traces of transmutation.

There is yet another means of transmutation, which, however, is beyond our control. There is a very penetrating radiation in the earth's atmosphere, known as *cosmic rays* or *ultra-radiation*. The effect of this radiation can be observed even after passage through many feet of water. It is supposed by some to consist of electrons and protons of energy from 200,000,000 to 2,000,000,000 volts. The origin of these rays is still a mystery, though many theories have been advanced. Jeans believed that cosmic radiation may be due to the annihilation of hydrogen and helium atoms. Particles possessing the energy mentioned above should be extraordinarily effective as firing particles in bringing about transmutation. Such transmutation has been observed by Messerschmidt, and is probably going on every day around us. It would account for the existence of numerous isotopes, such as the O^{17} isotope, which possibly is formed from nitrogen as follows :—

$$N^{14} + He^4 = O^{17} + H^1.$$

Summing up, the artificial disintegration of the elements can be brought about by bombardment of the atom with α-rays, positive rays, or protons, deuterons, α-rays, helium nuclei, and neutrons. The processes are reversible and take place according to the general equations

$$A + \alpha \rightleftharpoons B + H^+,$$

or

$$A + \alpha \rightleftharpoons B + n.$$

There is thus in the nucleus an exchange of a helium nucleus with a proton, or with a neutron.

In all these processes, the disintegration apparently stops when the bombarding particles are switched off, but Curie and Joliot discovered an artificial radioactivity when certain elements are disintegrated. The radioactive elements themselves possess unstable nuclei, and the latter break down according to an exponential law. When aluminium is bombarded with polonium α-rays, the final product is the silicon nucleus of mass 30 and charge 14, together with neutrons and positive electrons :—

$$Al^{27}_{13} + He^4_2 \rightarrow Si^{30}_{14} + n + e^+.$$

The top figures indicate masses, the lower ones charges.

When the bombarding α-rays are removed, evidence of the emission of positive electrons can still be obtained. Meitner has actually photographed them nine minutes after the bombarding rays had been switched off, using the cloud-chamber method. There is evidence that the primary change in this disintegration is

$$Al^{27}_{13} + He^{4}_{2} \rightarrow P^{30}_{15} + n.$$

The P^{30} nucleus is unstable, and breaks down like the nucleus of a radioactive atom, according to the equation

$$P^{30}_{15} \rightarrow Si^{30}_{14} + e^{+}.$$

This change occurs even when there is no bombardment taking place; it is an artificial radioactive change, and follows the exponential law for decay.

Similarly Meitner has photographed the emission of positive electrons from boron twelve minutes after exposure to polonium α-rays. The total change here is

$$B^{10}_{5} + He^{4}_{2} \rightarrow C^{13}_{6} + n + e^{+},$$

but the primary change is doubtless

$$B^{10}_{5} + He^{4}_{2} \rightarrow N^{13}_{7} + n,$$

with the radioactive disintegration of the unstable nitrogen nucleus according to the equation

$$N^{13}_{7} \rightarrow C^{13}_{6} + e^{+}.$$

It has also been found possible to make elements of atomic numbers 93 and 94 artificially by bombarding uranium with neutrons under certain conditions. These elements have, in general, the properties associated with the other elements in their particular groups in the periodic table and are called neptunium and plutonium, respectively.

Fermi has shown that slow neutrons can react with almost all nuclei, giving, in most cases, radioactive products.

A very large number of nuclear reactions have now been studied, and it is impossible in a general text-book to mention any of them in detail. A list of nuclear reactions giving rise to artificial radioactivity which have been investigated up to 1941 will be found in *A Treatise of Physical Chemistry, Vol. I.*, edited by Taylor and Glasstone (Macmillan).

43. The Detection of Atomic Transmutation.—In the early work on atomic transmutation the amounts of the products were so small as to be unweighable and even too minute to respond to chemical tests. Although a few elements have now been obtained by this method in quantities large enough to admit of chemical identifica-

tion, and even to enable their properties to be studied, the majority of the products are identified by physical methods.

Fast-moving charged particles are capable of ionising molecules of gases. This ionisation can be detected in a number of ways. One method is by means of the Wilson cloud-chamber already described (§ 26). This is very largely used because not only does it enable the existence of particles to be detected, but a quantitative estimate of their mass can be obtained from the length of the tracks.

Other apparatus for detecting and measuring ionisation are the various types of " counter." The Geiger-Müller counter consists essentially of a wire surrounded by a tubular electrode in an ionisation chamber. When fast-moving ionising particles enter the chamber they produce primary ions in the gas in the chamber. If the potential difference between the wire and the electrode is sufficiently great, the primary ions produce a large number of secondary ions, and a discharge is initiated in the gas. This means that a current flows between the electrodes, and can be detected in the usual way. The current would, however, continue indefinitely once the discharge was started, and some method has to be adopted to " quench " it. There are various ways of doing this which need not be entered into here.

A modification of the Geiger-Müller counter is the proportional counter which is so arranged that the total number of ions produced is proportional to the number of primary ions formed. It is actually possible with this apparatus to distinguish between ionisation produced by different types of particles.

Neutrons, of course, cannot be detected directly by means of ionisation, as, being uncharged, they are unable to produce ionisation in a gas. However, the ionisation method can still be used indirectly. The neutrons are made to bombard atoms, usually boron, when an alpha particle and a lithium nucleus are produced. These have sufficient energy to bring about ionisation in an ionisation chamber or counter.

Another method of measuring neutron densities is to use the neutrons to produce artificially radioactive nuclei and then measure the degree of activity of the product.

43a. Energy Considerations.—The question of whether it is possible to use atomic energy for industrial purposes has often been debated, and statements have sometimes been made that if the energy inherent in the atom were liberated there would be catastrophic destruction. The difficulty is to liberate the energy.

It has already been stated that the particles making up the nucleus of elements may be packed in different ways so that the total mass is not necessarily the sum of the masses of the constituent

protons and neutrons. It has also been stated (p. 3) that there is no law of conservation of mass, but a law of conservation of mass and energy taken together. If, then, the nucleus of an atom could be made up from its constituent parts, and its total mass were less than the sum of the masses of these parts, the difference would be radiated as energy. It has not been possible to build up nuclei in this way, but it has been possible, by the methods outlined above, to change nuclei into others. In these cases it might well happen that the sum of the masses of the interacting particles was greater than the sum of the masses of the products, in which case energy would be made available.

To take a simple example. The bombardment of lithium with energetic protons gives rise to helium nuclei, the reaction being

$$Li_3^7 + H_1^1 \rightarrow 2He_2^4$$

The mass of Li^7 is 7·01818, of H^1 1·00813, and of He^4 4·00389 The total mass on the left hand side is thus 8·02631 units, and on the right 8·00778 units. Hence 0·01853 units of mass have disappeared and will be transformed into energy.

If we deal in grams 0·01853 gm. of mass disappear for every 8·00778 gm. of helium produced. To find out the energy corresponding to this loss of mass we use the Einstein energy relation

$$E = mc^2$$

where E is the energy, m is the mass, and c is the velocity of light. Substituting 0·01853 gm. for m and 3×10^{10} cm. per sec. for c

$$\begin{aligned} E &= 0{\cdot}01853 \times 9 \times 10^{20} \text{ ergs} \\ &= 0{\cdot}16677 \times 10^{20} \text{ ergs} = 4{\cdot}63 \times 10^5 \text{ kilowatt hours.} \end{aligned}$$

Thus, a very considerable amount of energy is set free. It is, of course, attached to the helium atoms formed, which move away with this energy. This has been verified experimentally, and is a strong confirmation of the truth of the Einstein relation.

The question arises as to whether this energy is economically worth tapping, and, if so, how it can be utilised. In the case of a simple nuclear reaction like that quoted above, considerable energy has to be used to impart sufficient energy to the protons to enable them to penetrate the lithium nucleus and interact with it. Even then, very few of the accelerated protons actually collide with lithium nuclei. There is thus a considerable waste of energy, and it would actually be unprofitable to utilise reactions similar to the above for the production of atomic energy.

As has been mentioned, neutrons are more effective than other particles in bringing about nuclear reactions, and it might be expected that better results would be obtained in this case. The

trouble here is that neutrons are difficult to produce. They may be obtained by the action of α-rays from radium on beryllium, but radium is very expensive; they can also be produced by bombarding light elements with ion beams. In this case we have the same difficulty as before, namely, that few ions are effective in producing neutrons, and the process would use up more energy than it produced.

The whole difficulty has been overcome by the discovery of a nuclear reaction in which neutrons are actually produced. These are able to transform neighbouring nuclei when more neutrons are emitted. Such a reaction is called a chain reaction.

43b. Nuclear Fission.—In 1939 Hahn and Strassmann showed that when uranium was bombarded with neutrons the nucleus broke up into smaller fragments. Earlier work had given rise to the idea that neutron capture by uranium led to nuclei of greater atomic number, *i.e.*, elements outside the usual periodic table, with atomic numbers 93 and 94. This is what happens in the usual case when the lighter elements are bombarded with neutrons. In the case of uranium, however, it was shown that breakdown (or fission) of the nucleus occurs with formation of isotopes of barium and other elements, particularly strontium and yttrium. The uranium nucleus thus splits into two portions, and it has been shown that neutrons are emitted, the estimated number being 3 per fission.

Uranium, as it occurs naturally, is a mixture of several isotopes. The products of neutron bombardment vary from one isotope to another, and also with the energy of the neutrons. It is the isotope of mass 235 which yields the best results.

Nuclear fission has also been observed with thorium, and the transuranic elements neptunium and plutonium (§ 42). α-rays, deuterons, and α-particles will also give rise to fission though they are less effective than neutrons.

43c. Utilisation of Atomic Energy.—Since neutrons are emitted in the fission of uranium there is the possibility of a chain reaction, and hence of the utilisation of the atomic energy liberated on an economic basis. For this purpose, it is necessary to ensure that the liberated electrons are not lost from the system before a reasonable number of them have interacted with further nuclei and have thus replaced themselves. Slow neutrons are more effective in the fission than rapid ones, and so it is necessary to slow down the secondary neutrons formed as a result of the initial bombardment. This is done by mixing graphite with the uranium. Also U^{235} is the effective nucleus. If other isotopes are present these will capture neutrons and they will be lost. Hence pure U^{235} must be used. It is also necessary to use a sufficient mass of U^{235} to prevent loss of neutrons.

These difficulties have been overcome and the utilisation of atomic energy in warfare is now an accomplished fact. There is no great difficulty in using the same fission process for ordinary industrial power, although at present the process is expensive.

43d. The Positive Electron, or Positron.—Besides the neutron, another particle, the positive electron, has been discovered. During the study of cosmic radiation by the cloud-chamber method, some of the particles were found to be deflected in an opposite direction from that suffered by the negative electrons, when a magnetic field was applied (Anderson, *Science*, 1932, **78,** 238; Blackett and Occhialini, *Proc. Roy. Soc.*, 1933, *A*, **139,** 699). The particles must therefore bear a positive charge. They can also be produced by the bombardment of matter by hard γ-rays, and by neutrons. The charge and the mass of the particle have been obtained from a study of the ionisation that it produces when passing through a gas. Anderson has shown that the difference in ionising powers of fast positive and negative electrons is certainly less than 20 per cent. The mass of the positive electron has been deduced by Blackett to be $1{\cdot}04 \pm 0{\cdot}14$, if the mass of the negative electron is taken as 1.

It is obvious, then, that we are here dealing with a positive particle smaller than the proton, yet bearing the charge of the proton. It has been customary to regard the proton as the elementary positive charge, but it seems likely that this place is taken by the positive electron.

The positive electron cannot exist for long far outside the nucleus, and it is extremely probable that its expulsion is accompanied by the simultaneous expulsion of a negative electron.

43e. The Meson.—Another particle present in cosmic radiation is the meson, or heavy electron. It was discovered during experiments on the penetrating component of cosmic rays. It was calculated that even very rapidly moving electrons would be quickly absorbed by lead, the range being at the most 1 cm. Actually, at sea-level a large number of penetrating particles in cosmic rays can traverse 100 cm. of lead before absorption. It has been shown by observation of the tracks of these particles when slowed down that they are many times heavier than the electron, though not as heavy as the proton. They can have either a positive or a negative charge, and are called mesons (meaning particles of intermediate mass).

It should be mentioned that the existence of the meson was predicted by the Japanese scientist Yukawa in 1935, during a mathematical investigation of the theory of β-decay. It was actually discovered by Anderson, two years later.

43f. The Neutrino.—Considerations of the angular momentum of the nucleus lead to the conclusion that if the laws of conservation of

energy and of momentum are to hold, the existence of a new particle, called the neutrino, must be postulated. It is very light, at least as light as the electron, and has no charge. Fermi, indeed, ascribes to it a zero rest-mass.

Experiments to detect the neutrino directly have so far failed. This is not surprising in view of its exceedingly small mass and lack of charge. It is claimed, however, that experiments on the recoil of atoms emitting β-rays, indicate its existence (Allen, 1942).

SUMMARY

The Laws of Electrolysis, discovered by Faraday, led to the conception of the atomic nature of electricity. This view was confirmed by a study of the conduction of electricity by gases. In a highly evacuated tube, and under a high potential, cathode rays may be produced, which consist of negatively charged particles for which the ratio of the charge to the mass has been determined by several methods. The cathode rays are made up of elementary negative charges of electricity, called electrons. Positive rays are also formed in the discharge tube, being shot off from the anode. X-rays are produced when cathode rays strike any material object. They are much more penetrating than cathode rays, and consist of a wave-motion of very small wavelength. Certain heavy elements, called radioactive elements, are found to disintegrate spontaneously, giving rise to one or more of three radiations, known as α-, β- and γ-rays. By the action of a magnetic field upon them, it has been shown that α-rays are positively charged (further work shows them to be helium nuclei), β-rays are negatively charged (they are electrons), and γ-rays are very short wavelength X-rays.

The charge on the electron has been determined by a number of experiments, the best of which is Millikan's oil-drop method ($e = 4{\cdot}774 \times 10^{-10}$ e.s.u.). From this result Avogadro's Number, the number of molecules in one gram-molecule of a substance, can be obtained (6·062 × 10).^{23} The bombardment of matter by α- and β-rays leads to the conclusion that the atom is composed of a nucleus of protons and neutrons (the proton being a particle bearing the unit of positive charge), but with a nett positive charge, this nucleus being surrounded by electrons sufficient in number to neutralise the positive charge on the nucleus. This is confirmed by a study of radioactive disintegrations, which also show that two or more elements may occupy the same position in the Periodic Table, and yet be different in physical properties and atomic weight. These are called isotopes.

By studying the X-ray spectra of the elements, Moseley determined the number of extra-nuclear electrons in various atoms (the atomic number). Almost every element consists of a mixture of isotopes. By analysing the positive rays emitted by the elements, J. J. Thomson, Aston and Dempster have been able to determine the masses of the isotopes, and the proportions in which they occur in the various elements. The masses are not exactly whole numbers, owing to the "packing-fraction." A knowledge of the latter, together with the relative abundance of the isotopes in a given element, enables an estimate of the atomic weight of the element to be made, which agrees very well with the chemical value. It is a matter of great difficulty to separate

isotopes, but this has been done partially for several elements, and completely in the cases of neon and hydrogen. The discovery of the hydrogen isotope in the residues from the fractionation of liquid hydrogen is of great importance, especially in stoichiometry. By firing α-particles, accelerated protons, hard γ-rays, and other radiation of high energy content, into elements, it has been found possible to bring about a disintegration of the nucleus in many cases, with the consequent formation of a new element. When beryllium is bombarded with rapid α-particles from polonium, a very penetrating radiation, consisting of particles of mass 1, and charge 0, is emitted. These particles are called neutrons. The neutron is an important constituent of the atomic nucleus. When certain elements are bombarded with hard γ-rays, or by cosmic radiation, positive electrons are emitted. These are particles of mass equal to that of the electron, but bearing a positive charge, equal in quantity to that of the negative electron. Other elementary particles are the meson and the neutrino.

SUGGESTIONS FOR FURTHER READING

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QUESTIONS

(1) How does a knowledge of the Laws of Electrolysis lead to the conception of the discrete nature of electricity? How has the charge on the electron been determined?

(2) What radiations are given off from radium? How is the nature of each radiation confirmed, and how does the radiation fix the nature of the element formed by the disintegration?

(3) How is it known that the electron is an elementary constituent of all matter?

(4) Describe the historical development of the nuclear theory of the atom.

(5) What is an isotope? What experiments have been made in an endeavour to separate isotopes?

(6) Write an essay on atomic transmutation.

(7) What do you understand by the "physical" atomic weight of an element? How may it be determined?

(8) What was Prout's Hypothesis? Discuss it from the point of view of our modern conception of the structure of the atom.

(9) What is meant by a radioactive series? Explain what happens with regard to the structure of the atom when disintegration takes place.

CHAPTER III

ATOMIC STRUCTURE—PART II

44. The Quantum Theory.—To understand the origin of the quantum theory it is necessary to consider briefly the nature of radiation, of which one form is visible light. Newton regarded light as being made up of corpuscles, but this view was incapable of explaining many of the properties of light, such as interference, diffraction, and refraction. To give a satisfactory explanation of these phenomena, the wave-theory of light was formulated by Huygens. This assumed that light was a wave-motion, and did not involve the transfer of any material particle from one place to another. The colour of the light was dependent upon the wave-length. Fig. 40 represents an instantaneous state of a light wave. Actually the wave is progressing all the time. The distance AB is the wavelength.[1] The theory was greatly developed by Clerk Maxwell, who propounded the electromagnetic theory of radiation, of which, however, no detailed account can be given here.

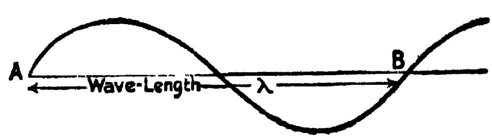

FIG. 40.

Although the wave-theory of light explained many facts in a very satisfactory way, and appeared to be firmly entrenched at the end of the nineteenth century, there were some phenomena for which it could offer no explanation, and the most troublesome of these was the problem of *black-body radiation*. In order to understand this, it is necessary to know that radiation includes not only visible light, but also many radiations that are invisible, including ultra-violet light, *X*-rays, infra-red light, and wireless waves. Actually the range of wavelengths occupied by visible light is a very small fraction of the total range. All these radiations are supposed to be wave-motions, but the wavelengths are different. The infra-red

[1] The best definition of the term wavelength is the distance between two successive points of the wave with the same phase.

and wireless waves are of longer wavelength than that of ordinary visible light, whilst X-rays and ultra-violet light have smaller wavelengths. An idea of the range occupied by visible light is given in the following Table (XIV.).

TABLE XIV.—THE WAVELENGTHS OF RADIATIONS

Radiation.	Wavelength Å.
Wireless waves . . .	10^{14} to 4×10^7
Infra-red	3×10^6 to 7,230
Visible	7,230 to 3,970
Ultra-violet . . .	3,970 to 500
X-rays and γ-rays . .	10 to 0·03

(1 Å = 10^{-8} cm.)

The wavelength ranges of the various radiations are not strictly defined, those given in the Table being approximate only.

Now, radiation is present in any space of which the temperature is greater than the absolute zero (− 273·2° C.), and if a vessel, closed all but for a very small hole, is taken, it will give off radiation through the opening, dependent upon the temperature. It was shown by Kirchoff that the radiation from such an enclosure is the same as that from a perfectly black surface, and it is known as black-body radiation.

The analysis of a given radiation into wavelengths is termed its *spectrum*. For a given temperature of emission, black-body radiation will have a definite spectrum, and the radiation emitted of any specified wavelength will possess a certain amount of energy. The energy distribution throughout the spectrum is not constant, but rises to a maximum at a certain wavelength for each temperature. The problem of black-body radiation was to reconcile the energy distribution in the spectrum with the wave-theory, but this was found to be quite impossible.

It was to overcome this difficulty, and others, that Max Planck boldly proposed the quantum theory, in a paper published in 1900. He showed that the experimental observations on black-body radiation could be explained by supposing that energy may be emitted or absorbed by a vibrating body, not continuously, but only in multiples of a certain unit, called a *quantum*. Furthermore, the size of the quantum of energy was proportional to the frequency of the radiation (velocity divided by wavelength), and was therefore

equal to $h\nu$, where ν is the frequency, and h a universal constant, known as Planck's constant, equal to $6{\cdot}554 \times 10^{-27}$ erg-seconds.

Let us see exactly what this means. Light is emitted by a vibrating body. Actually we know that it arises from the vibrating atom, or parts of the atom which are vibrating. The energy that is emitted in the form of radiation cannot be *any* amount of energy, but must be an integral number of quanta. The amount of energy in each quantum will be proportional to the frequency of the light, and, therefore, inversely proportional to the wavelength. The smaller the wavelength, the greater will be the frequency, and the greater the energy associated with each quantum. The quantum of X-rays, which have a very small wavelength, will therefore be greater than that of visible light. The size of the quantum for radiations of different wavelength is given in Table CXVII. (Chapter XIX.).

The conception of the quantum of energy has not quite the same significance as that of the elementary particle of electricity, the electron. The electron always has the same charge, no matter where or how it occurs, but the quantum varies in size with the type of radiation with which it is associated, being comparatively large for X-rays and the ultra-violet, and small for the infra-red and wireless waves.

Since the quantum theory was proposed, numerous cases of the failure of the classical electromagnetic theory of Clerk Maxwell, which used the Newtonian mechanics, have been noted. The quantum theory has found its most useful application in the case of atomic structure.

45. Spectra.—Before proceeding further with the problem of atomic structure, we must note the various types of spectra that may be obtained, as a study of spectra has yielded most important results in the elucidation of the nature of matter.

When a body is heated from the absolute zero, it emits radiation. At low temperatures this is not visible. The body, if it were in a perfectly black space so that no radiation could get to it from the outside, would appear quite black. Nevertheless, it is giving off heat rays, which appear in the infra-red. As the temperature is raised, the solid begins to glow, and finally becomes incandescent, *i.e.*, it emits, amongst other radiation, visible light. If this light is examined by means of a spectrometer (for a description of which a text-book of Physics should be consulted), the spectrum is found to be continuous, *i.e.*, it is impossible to say where one colour begins and the other ends. There is a continuous gradation throughout the spectrum, from the violet end to the red. All incandescent solids show a continuous spectrum. The spectrum of the light from an

electric lamp, for example, is a continuous one, because the light is emitted from an incandescent metal—the filament.

When the light emitted from incandescent gases and vapours is examined in the same way, it is found that the spectrum is now no longer continuous, but consists of sharply defined lines in different colour regions of the spectrum. This is called a line-spectrum, and is characteristic of atoms. The spectrum may also consist of bands extending over a certain range of wavelength, separated by black bands. This is a band-spectrum, and is characteristic of molecules. The bands often show a periodic variation in intensity, and thus appear fluted.

The fact that when gaseous elements are raised to incandescence a line-spectrum is produced, has been known since about 1860, and has, of course, been applied in spectrum analysis to the characterisation of elements and the discovery of new ones. When sodium chloride is heated on a platinum wire, a yellow light is emitted, which on examination with the spectrometer, is found to possess a very simple structure, being made up of two lines very close together, of wavelengths 5889·965 Å, and 5895·923 Å. These lines are not the spectrum of incandescent sodium chloride, but that of sodium vapour. The heat of the flame dissociates the salt into its elements, and each atom emits separately. The chlorine is also radiating, but its spectrum is not observed with the spectrometer, as it falls outside the visible region, in the ultra-violet. That the yellow lines are indeed due to the sodium atom is shown quite clearly by the fact that they are obtained when any sodium salt is heated as described.

When the heat of a flame is not sufficient to break down the salt, an electric arc may be used. Thus, to obtain the spectrum of iron, the electric arc is passed between two iron rods, and the spectrum is examined. Such a spectrum is called an arc-spectrum, but is not quite so simple as that obtained by the previous method, as besides the normal iron atoms, there are also iron ions, produced by the arc, which themselves have a characteristic spectrum. An ion is produced from a normal atom by the removal of one or more electrons, thus leaving the atom positively charged.

To obtain the spectrum of a substance which is a gas at ordinary temperatures, *e.g.*, oxygen, the gas is enclosed in a discharge tube, and the electric discharge passed through it. Here, again, the spectrum obtained is not the simple line spectrum due to the atoms of oxygen alone. The passage of the discharge produces oxygen ions, which radiate their own spectrum, and there will also be the band spectrum due to oxygen molecules. The lines belonging to any one species can, however, be picked out in the spectrum.

All the types of spectra so far described are caused by the emission of radiation, and are classed under the general heading of emission spectra. There is, however, another type of spectrum of great importance, known as the absorption spectrum. When white light is passed through a coloured solution, or vapour, and the spectrum is then studied, it is found that there are black bands in the otherwise continuous spectrum. The light of wavelength corresponding to the black bands has been absorbed by the substance through which the light has passed. The absorption spectrum is connected with the chemical constitution of the substance, and will be dealt with more fully in Chapter V. (p. 268).

46. The Quantum Theory and the Structure of the Atom.—Some two years after Rutherford had brought forward the nuclear theory of the atom, which we have already discussed (§ 29), Niels Bohr (1913) showed that this model of the atom was unstable, and could not exist. It will be remembered that, in the case of the Thomson model, the forerunner of the Rutherford nuclear atom, the electrons were supposed to be placed in a sphere of uniform positive electrification, and were at rest. Now this model is quite sound from the point of view of mechanics. It can be shown experimentally, that if one of the negative charges in this model is displaced from its position of rest, it will return to it again. The Rutherford atom, however, consists of a mass having a positive charge, with electrons revolving round it in a sort of solar system. Rutherford assumed that the same forces which keep the earth in its orbit round the sun would serve to keep the electron in its orbit round the nucleus. This simple view of the atom is too indefinite when examined from the quantitative point of view. The electron is not simply a solid body. It has an electrical charge. Clerk Maxwell had shown some time previously that when an electric charge is accelerated, radiation is emitted. Whenever a body moves in an orbit, it is being accelerated towards the centre of the orbit. This acceleration is shown by the existence of the centrifugal force. The electron, then, is being continually accelerated towards the centre of the orbit, and must therefore be emitting radiation. Since, according to the theory, the motion is uniform, the spectrum should show no discontinuities, and the spectrum of an incandescent atom should be continuous. It is actually discontinuous. The Rutherford theory, then, fails to explain the facts.

Bohr propounded a theory which explains the phenomena very well indeed, and is based on Planck's conception of the quantum. There are two fundamental suppositions. They are :—

(1) For each atom there is a series of orbits in which the electrons rotate, but no radiation is emitted. These are called *stationary*

states. It must not be thought that the electrons are stationary. They are not, but the effect is as if they were, for no radiation is given out. A stationary state is characterised by the fact that the angular momentum of the electron is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant. This is an extension of the original conception of Planck in quantising the energy of a vibrator.

In order that the student may make himself thoroughly familiar with this first assumption, we may use it to calculate the radii of the permitted orbits in the hydrogen atom. In the hydrogen atom, we have one electron and one proton. Let the charge on the electron be $-e$, and its velocity, v cm. per sec. If the orbit is supposed circular, and of radius r, the centrifugal force, F_1, is given by

$$F_1 = \frac{mv^2}{r}.$$

This must be equal to the force of attraction between the proton and the electron, which is given by Coulomb's inverse square law

$$F_2 = \frac{e^2}{r^2},$$

assuming that this Law is still true at atomic distances.

Hence $$\frac{mv^2}{r} = \frac{c^2}{r^2},$$

or $$e^2 = mv^2r \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

According to Bohr's assumption, the angular momentum of the electron is always some integral multiple of $\frac{h}{2\pi}$. Hence

$$mvr = \frac{nh}{2\pi} \qquad (2)$$

From (2) $$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}.$$

Substituting in (1), $$e^2 = \frac{n^2h^2}{4\pi^2mr},$$

or $$r = \frac{n^2h^2}{4\pi^2me^2}.$$

Since every quantity on the right-hand side of this expression, with the exception of n, is fixed, it follows that the radii of the permitted orbits are proportional to the squares of the natural numbers. By substituting the accepted values of h ($6{\cdot}554 \times 10^{-27}$ erg-seconds), m ($8{\cdot}98 \times 10^{-28}$ gm), and e ($4{\cdot}774 \times 10^{-10}$ e.s.u.), and making $n = 1, 2, 3$, etc., we obtain the radii of the orbits :—

$$r_1 = 0{\cdot}53 \times 10^{-8} \text{ cm.}, \; r_2 = 2{\cdot}12 \times 10^{-8} \text{ cm., etc.}$$

There are so many assumptions in this calculation that it probably

has no physical significance, but it is merely given to illustrate the meaning of the first Bohr postulate.

(2) The second assumption is that when an electron passes from one orbit, of energy E_1, to another of energy E_2, monochromatic radiation (*i.e.*, radiation of one wavelength only) of frequency ν is emitted or absorbed, equal in amount to $h\nu$. Thus, when an electron rotating in one of the stationary states suddenly jumps to another, of less energy, the difference in the energy is given out in the form of monochromatic radiation. The reverse process takes place when energy is absorbed. The absorption of radiation results in the transfer of an electron from a level of low to one of higher energy content. The mathematical expression of this assumption is

$$E_1 - E_2 = h\nu.$$

It must be remembered that these two assumptions are separate and distinct. The first has to deal with the energy of the rotating electron, the second with the energy difference between two states.

The term *energy level* is frequently used to denote a stationary state, and the energy content is defined by a *quantum number*. The level of quantum number 1 has least energy.

To clarify our ideas on the emission and absorption of energy by an atom, consider what happens to, say, hydrogen atoms when they are submitted to the electric discharge. They first of all absorb energy from the discharge, and this moves the electrons from an inner energy level, of low energy, to outer ones of higher energy. The electrons then return to the form containing lowest energy (for, of all systems, that which possesses the least energy is the most stable) by jumps, passing through each of the intermediate energy levels, or perhaps by only one jump. Each transition is accompanied by a liberation of energy in the form of radiation, and as each emission is monochromatic, lines in the spectrum will result. This explains the line spectrum of the atoms.

47. The Spectrum of Hydrogen.—It is now necessary to study a subject which in itself is purely physical, and which at first sight would seem to be of no interest at all to the physical chemist. Yet a study of the spectrum of hydrogen has yielded results of extraordinary importance in connection with the structure of the atom.

As far back as 1885, Balmer noticed that the wavelengths of certain lines in the hydrogen spectrum were related to each other in a simple manner, and could be expressed by a general formula. In this connection we shall deal not with the wavelength, but with its reciprocal, which is called the *wave-number*. It is the number of vibrations per cm., and may be denoted by ν_e. ν_e is often loosely called a frequency.

Balmer's formula, which gives the frequencies of some of the hydrogen lines may be expressed in the form

$$\nu_0 = 109678{\cdot}8\left(\frac{1}{2^2} - \frac{1}{m^2}\right),$$

where m can have any integral value greater than 2. As m approaches ∞, the lines will get closer and closer, and approach a limit known as the *convergence frequency*. This frequency is obviously $\frac{109678{\cdot}8}{4}$, *i.e.*, 27419·7. The following Table shows how closely the observed and calculated wave-numbers agree.

TABLE XV.—BALMER'S SERIES

$$\nu_0 = 109678{\cdot}8\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$$

m.	ν_0 calc.	ν_0 obs.
3	15233·2	15233·2
4	20564·8	20564·8
5	23032·5	23032·5
6	24373·0	24373·1
7	25181·4	25181·3
8	25706·0	25706·0
20	27145·5	27145·2
∞	27419·7	—

Other series in the spectrum of hydrogen have since been discovered which are governed by exactly similar formulæ. Thus. Lyman found that a certain series in the hydrogen spectrum could be expressed by the equation

$$\nu_0 = 109678{\cdot}8\left(\frac{1}{1^2} - \frac{1}{m^2}\right).$$

This series of lines is in the far ultra-violet. A similar series in the infra-red, for which the formula was discovered by Paschen, is governed by

$$\nu_0 = 109678{\cdot}8\left(\frac{1}{3^2} - \frac{1}{m^2}\right).$$

Another series was discovered by Brackett, and is governed by

$$\nu_0 = 109678{\cdot}8\left(\frac{1}{4^2} - \frac{1}{m^2}\right).$$

All these series are called after the names of their discoverers, the

Balmer, Lyman, Paschen and Brackett series. Actually there is one formula which will express them all, viz.,

$$\nu_0 = \frac{109678 \cdot 8}{n^2} - \frac{109678 \cdot 8}{m^2}.$$

In the Lyman series, $n = 1$, and $m = 2, 3, 4$, etc.
In the Balmer series, $n = 2$, and $m = 3, 4, 5$, etc.
In the Paschen series, $n = 3$, and $m = 4, 5, 6$, etc.
In the Brackett series, $n = 4$, and $m = 5, 6, 7$, etc.

The two sections of the above equation are called *terms*. Thus $109678 \cdot 8/n^2$ is one term, whilst $109678 \cdot 8/m^2$ is the other. It has been found that all spectra, not only of hydrogen, but of all elements, can be expressed as a difference of two terms similar in form to the above.

It is evident from this formula, that if we write down the values of the first term when $n = 1, 2, 3, 4$, etc., then, if we subtract the second, third, fourth, etc., terms from the first, we get the Lyman series; if we subtract the third, fourth, fifth, etc., from the second, we get the Balmer series; if we subtract the fourth, fifth, sixth, etc., from the third, we get the Paschen series; and if we subtract the fifth, sixth, seventh, etc., from the fourth, we get the Brackett series. This is shown in the following Table (XVI.).

TABLE XVI.—HYDROGEN SERIES

	Term.	Lyman.	Balmer.	Paschen.	Brackett.
		$n = 1$ $m = 2, 3, 4 \ldots$	$n = 2$ $m = 3, 4, 5 \ldots$	$n = 3$ $m = 4, 5, 6 \ldots$	$n = 4$ $m = 5, 6, 7 \ldots$
1	109678·8				
2	27419·7	82259·1			
3	12186·5	97492·3	15233·2		
4	6854·9	102823·9	20564·8	5331·6	
5	4387·2	105291·6	23032·5	7799·3	2467·7
6	3046·7	106632·1	24373·0	9139·8	3808·2
7	2238·3	107440·5	25181·4	9948·2	4616·6
8	1713·7	107965·1	25706·0	10472·8	5141·2
∞	0	109678·8	27419·7	12186·5	6854·9

The fact that so many spectral lines, which at first sight seem to be totally unrelated, can be reduced to order in this simple way, is a remarkable fact; and when we consider that this has now been done for the spectra of almost all elements, though not with the same completeness as for hydrogen, it is seen what a wealth of

information we possess in connection with spectra. It is to be expected that such a simple relationship between the spectral lines must have some relatively straightforward explanation. It has, and it will be shown later how this explanation is bound up with the structure of the atom.

The mathematical expression for the series of the spectral lines of elements is not always quite so simple as that for hydrogen, though it is usually not much more complex. A formula such as Rydberg's

$$\nu_0 = A - \frac{R}{(m + \mu)^2}$$

will frequently cover the series where the simple Balmer expression fails, or, if this is unsuitable, the slightly more complex equation of Hicks may be used.

$$\nu_0 = A - \frac{R}{\left(m + \mu + \frac{\delta}{m}\right)^2}$$

It should be noticed that both these formulæ consist of two terms as before, the first, A, being constant for the series. R is a universal constant, called Rydberg's constant, and is equal to 109,737, being almost exactly equal to the first term of the hydrogen series. μ and δ are small arbitrary constants, whilst m can have any integral value.

48. The General Nature of Spectra.—As a rule, the arc or spark spectrum of an element contains four sets of lines which are distinguished by their nature. They are called the Sharp, Principal, Diffuse and Fundamental series. The Sharp series is made up of clear-cut thin lines. The Principal series is usually the brightest. The Diffuse series is made up of diffuse lines, *i.e.*, lines without very definite edges. The Fundamental series is rather badly named, as it is not by any means fundamental.[1] Sometimes the Diffuse is called the First Subordinate series, and the Sharp the Second Subordinate series, though the names first given are more usually used.

These series are simply related to each other, and are usually referred to by the initial letter of the name, *i.e.*, the S, P, D and F spectra.

They are also expressed by formulæ similar to the Rydberg formula. The Table below gives the Sharp and Principal series of lithium.

It is to be noted that the convergence frequency of the Sharp series (obtained by putting m equal to infinity), is almost equal to the first term of the Principal sequence,[2] and that similarly the first

[1] This series is also sometimes known as the Bergmann series.

[2] The word "series" is used when referring to observed lines, and "sequence" when referring to terms.

TABLE XVII.—SHARP AND PRINCIPAL SERIES OF LITHIUM

Sharp Series $\nu_0 = 28{,}611 - \frac{109{,}737}{(m + 0{\cdot}590)^2} = 28{,}611 - mS = 1P - mS$				Principal Series $\nu_0 = 43{,}477 - \frac{109{,}737}{(m + 0{\cdot}959)^2} = 43{,}477 - mP = 1S - mP$			
m	mS	ν calc	ν obs	m	mP	ν calc.	ν obs
1	43,407	—	—	1	28,594	14,883	14,904
2	16,359	12,252	12,302	2	12,533	30,944	30,926
3	8,515	20,096	20,107	3	7,001	36,476	36,468
4	5,209	23,402	23,395	4	4,462	39,015	39,013
5	3,512	25,099	25,082	5	3,091	40,386	40,387
6	2,527	26,084	26,047	6	2,266	41,211	41,213
∞	—	28,611	—	∞	—	43,477	—

term of the Sharp sequence is almost equal to the convergence frequency of the Principal series. There are numerous relationships of this kind which have all received satisfactory explanation on the quantum model of the atom. If we call the successive terms of the Principal sequence $1P, 2P, 3P, 4P \ldots mP$, of the Diffuse sequence $1D$, $2D$, $3D$, $4D$, . . . mD, and similarly for the other sequences, these relationships can be summed up in the equations :—

Sharp Series	$\nu_0 = 1P - mS$
Principal Series	$\nu_0 = 1S - mP$
Diffuse Series	$\nu_0 = 1P - mD$
Fundamental Series	$\nu_n = 1D - mF.$

It will be seen that these relationships express what has been already discovered with regard to the convergence frequencies of the Sharp and Principal series, and they also show that the convergence frequency of the Fundamental series is the first term of the Diffuse sequence.

Many of the lines in a spectrum can be explained in this way, but there are some which are still unaccounted for. These are combination lines formed from terms from different sequences. It is not possible for lines to exist derived from any combination of terms at choice. There is an important selection principle which forbids certain combinations. If the terms are arranged in the order S, P, D, F, then the combination lines must always be due to terms taken from two adjacent sequences. Lines of the nature $3D - mF$ could exist, but not lines derived from $2P - mF$.

49. Multiplets in the Spectrum.—If the lines of a spectrum are very carefully examined with a spectroscope which gives high resolution, it is found that the lines are not single, but are made up

of a number of lines very close together. Sometimes there are only two. These are called doublets. If there are three they are called triplets ; and in general they are called multiplets.

If the wave-numbers of the first few members of the Sharp series of sodium are written down, it is found that they consist of doublets with a constant separation between each.

TABLE XVIII.—SODIUM DOUBLETS IN THE SHARP SERIES

m	ν_1	ν_2	$\nu_2 - \nu_1$
3	16,231	16,248	17
4	19,404	19,421	17
5	21,043	21,060	17
6	21,997	22,013	16

TABLE XIX.—RUBIDIUM DOUBLETS IN THE DIFFUSE SERIES

ν_1	ν_2	$\nu_2 - \nu_1$
12,887	13,121	234
15,872	16,107	235
17,463	17,699	236
18,405	18,641	236

Similarly, the Principal series of sodium is made up of doublets, but here the separation is not constant, but diminishes as we pass towards the ultra-violet, both series having the same convergence limit.

The explanation of this lies in the fact that there are two sets of P terms, but only one of S terms, so that if the two P terms are represented by P_1 and P_2, the Sharp series will be given by

$$\nu_1 = 1P_1 - mS$$
$$\nu_2 = 1P_2 - mS$$

The separation is thus constant and equal to $1P_1 - 1P_2$.

For the Principal series, however,

$$\nu_1 = 1S - mP_1$$
$$\nu_2 = 1S - mP_2.$$

Here the difference involves m, and so varies, until, when m is equal to infinity, the convergence limit is $1S$. The same type of relation-

ship holds for the Diffuse and Fundamental series, but it is always found that there is only one set of S terms, whilst the P, D and F terms may be complex, and give rise to multiplets.

50. The Theory of the Hydrogen Spectrum.—Bohr's assumptions as regards the structure of the atom have already been noted (§ 46). These may now be studied a little more closely.

The first assumption of Bohr was that the angular momentum of the electron was always an integral multiple of $\frac{h}{2\pi}$. Assuming that the electron travels in a circular orbit, and that its mass is m, its velocity v, and the radius of the orbit r, then its angular momentum is mvr, and the above assumption can be expressed in the form

$$mvr = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is any integer.

If Z is the atomic number of the element, and the charge on the nucleus is Ze, the potential energy of the electron will be $\frac{-Ze\,.\,e}{r} = \frac{-Ze^2}{r}$. The negative sign is prefixed because work is done on the system when the electron is removed from the nucleus to an infinite distance.

The kinetic energy of the electron is $\frac{1}{2}mv^2$. Assuming that the law of force between the nucleus and the electron is the inverse square law, and that the proportionality factor is unity, then the force between the nucleus and the electron will be $\frac{Ze^2}{r^2}$.

The acceleration of the electron towards the centre of the orbit is v^2/r, and the force on it is therefore mv^2/r.

Hence
$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the kinetic energy

$$\tfrac{1}{2}mv^2 = \frac{Ze^2}{2r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The total energy of the atom is the sum of the potential and kinetic energies, and is therefore

$$-\frac{Ze^2}{r} + \frac{Ze^2}{2r} = -\frac{Ze^2}{2r} = -\tfrac{1}{2}mv^2,$$

From (1)

$$\tfrac{1}{2}mv = \frac{nh}{4\pi r}.$$

Dividing into (3)

$$v = \frac{Ze^2 . 2\pi}{nh}.$$

The total energy is therefore

$$E_n = -\tfrac{1}{2}mv^2 = -\frac{2\pi^2 Z^2 me^4}{n^2h^2}\ ; \text{ or } E_s = -E_n = \frac{2\pi^2Z^2me^4}{h^2}\cdot\frac{1}{n^2}, \quad (4)$$

where E_s is the work which must be done on the system to remove the electron to infinity, and is therefore a measure of the stability of the system. The larger is E_s the more stable will the system be. For large values, n must be as small as possible; hence the most stable orbit is that in which n is unity.

We can now apply the second postulate of Bohr, viz., that when an electron jumps from one orbit to another energy is given out as a quantum of radiation. If it jumps from an outer (n_2) to an inner (n_1) orbit, energy is given out in the form of monochromatic radiation of which the frequency is given by

$$h\nu = E_{n_2} - E_{n_1}.$$

This amount of energy must be the difference in the energy associated with the orbits and worked out as above. Hence

$$h\nu = \frac{2\pi^2Z^2me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad . \ . \ . \ . \ . \ (5)$$

Now, ν is a frequency. It is easily seen that to bring this to wave-numbers, which are given by the equation $\nu_0 = \frac{\nu}{c}$, where c is the velocity of light, we must divide the frequency by the velocity of light, c. If ν_0 now represents wave-number,

$$\nu_0 = \frac{2\pi^2Z^2me^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad . \ . \ . \ . \ . \ (6)$$

This expression is identical in form with the Balmer formula, and when the value of the constant $\frac{2\pi^2Z^2me^4}{ch^3}$ is worked out, it is found to agree with the Rydberg constant.

Thus, substituting the value for $e = 4{\cdot}774 \times 10^{-10}$ e.s.u., $h = 6{\cdot}554 \times 10^{-27}$ c.g.s.u., $c = 3 \times 10^{10}$ cm. per sec., and $m = 8{\cdot}97 \times 10^{-27}$ gm., we have, for hydrogen, $Z = 1$,

$$\frac{2\pi^2Z^2me^4}{ch^3} = \frac{2\pi^2 \times 8{\cdot}97 \times 10^{-27} \times (4{\cdot}774 \times 10^{-10})^4}{3 \times 10^{10} \times (6{\cdot}554 \times 10^{-27})^3}$$

$$= 109{,}486,$$

which agrees quite well with the Rydberg constant determined experimentally, 109,678.

It is known that in the Lyman series, $n_1 = 1$. Referring to the

mode of derivation of equation (6) it is clear that this means that the lines of this series are due to transitions ending at the first orbit, the level of least energy. Thus, the Lyman series will be emitted when, energy having been imparted to the hydrogen atoms by the electric discharge, or some other means, they revert from the higher energy levels to which they have been raised to the first, or lowest energy level. The Balmer series has $n_1 = 2$, so the lines are due to electrons falling back to the second energy level. In the Paschen series $n_1 = 3$, and in the Brackett series $n_1 = 4$, so that here the electrons are returning from some outer orbit to which they have been removed by the excitation, to the third and fourth energy levels, respectively.

This remarkably simple and accurate formulation of the hydrogen spectrum points to the accuracy of the postulates upon which it is based, viz., Bohr's quantum model.

It is seen that the term numbers are really measures of energy. They represent the energy which would be required to remove an electron from the orbit which they represent to infinity ($n_2 = \infty$). The greatest term number is that obtained when $n_1 = 1$, and is therefore called the " ground " term. The electron can be removed to infinity, *i.e.*, the gas can be ionised, by several means, but particularly by subjecting the gas to bombardment by electrons. In an ideal case, supposing the loss of no energy whatever, the energy associated with the bombarding electron, which is just capable of knocking the electron from the ground state to infinity, must be the energy of that electron which is removed. Hence, if we can measure the energy of the electrons which will just ionise the gas, we have another measure of the energy of the electron in the atom. The energy associated with a bombarding electron is always measured by the potential which is used to accelerate it. The energy of the electron depends upon its velocity, being given, in fact, by the product of the charge and the accelerating potential through which it has passed. As the charge of the electron is always the same, it is sufficient to specify the accelerating potential which is given to the electron when it is desired to denote its energy. The ionisation potential of hydrogen is the potential through which a bombarding electron has to be accelerated in order to remove an electron from the atom to infinity. What this value should be for the ground term of hydrogen is readily obtained as follows. Let V be the ionisation potential, ν_0 the wave-number of the ground term, c the velocity of light, h Planck's constant, and e the charge on the electron. The energy associated with the term is $h\nu$ or $ch\nu_0$. The energy is *potential* $\times$ *charge*, hence the ionisation potential is given by

$$V - \frac{\text{energy}}{\text{charge}} = \frac{ehv_0}{e}.$$

This must be multiplied by 10^{-8} to bring the absolute units to volts, and by c to convert into electromagnetic units. So we have

$$V = \nu_0 \frac{c^2 h}{e} \times 10^{-8} = \frac{\nu_0}{8{,}100}.$$

For hydrogen, $\nu_0 = 109{,}678$, and substituting the other figures, we have

$$V = \frac{109{,}678}{8{,}100},$$

which gives

$$V = 13{\cdot}54 \text{ volts.}$$

The ionisation potential of hydrogen is therefore 13·54 volts, for

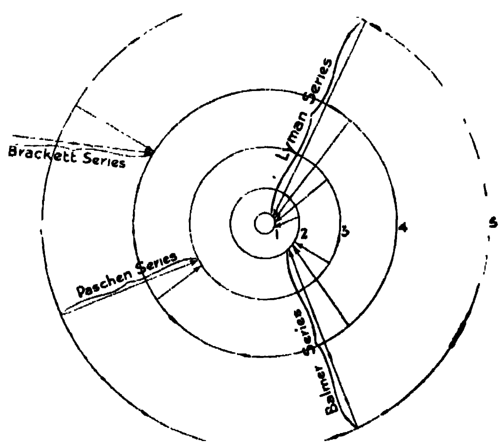

FIG. 41.—Stationary States in the Hydrogen Atom assuming circular orbits.
(The radii of the orbits are proportional to 1, 4, 9, 16 . . .)

removal of the electron from the ground term. Corresponding ionisation potentials are known for removal of ions from the other levels. In all cases the observed values agree well with those calculated.

The diagram (Fig. 41) shows the stationary states of the hydrogen atom, assuming that the orbits are circular. Another way of representing the facts is by means of the energy diagram given in Fig. 42.

51. General Theory of Spectra.—Hydrogen, the atom of which consists of one proton and a single electron, is the simplest instance

to consider. When the other elements, which contain larger numbers of electrons, are dealt with, the difficulties are considerably increased. With hydrogen, it is only a question of the removal of one electron into any desired stationary state, but with other atoms some of the innermost levels may be permanently filled with electrons. What happens in this case? If an electron is expelled from the innermost level altogether, its place is immediately occupied by an electron from one of the higher levels, and this goes on through successive levels, until the loss is really felt only in the outer level. If the electron is only removed to a level one or two higher in

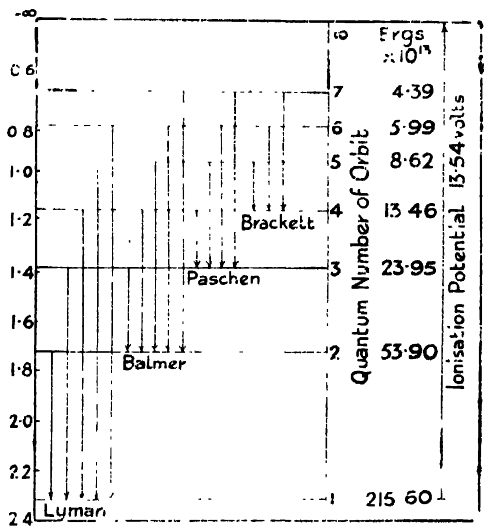

Fig. 42.—Energy Diagram for Hydrogen.
The arrows represent transitions from the various orbits.

quantum number, then an electron from that level immediately falls back into the place previously occupied.

The amount of energy associated with the innermost levels is so great that when an electron is expelled from these levels the frequency of the radiation emitted is very great. Thus $E = h\nu$, is large, and therefore ν, the frequency of the emitted radiation, is great, and such a transition gives rise to X-rays which are similar to ordinary light, but have extraordinarily small wavelengths, and correspondingly great frequencies. The study of these X-ray spectra of the elements has given us a great deal of information about the structure of the atom. Indeed, it was by the aid of these spectra that Moseley fixed the atomic numbers of the elements (§ 34).

The X-rays obtained from elements are grouped in wavelengths in certain groups which have been called the K, L, M, N, etc., groups. These groups are known to be due to transitions which end at the quantum levels 1, 2, 3, 4, etc., respectively. It is for this reason that the quantum levels themselves are frequently called the K, L, M, N, etc., levels.

From a study of the X-ray spectra the number of electrons present in each level can be roughly derived. All atoms will give a K radiation, only those heavier than sodium give the L radiation, and so on.

52. Quantum Numbers.—By the term quantum number we mean the integer which specifies the orbit as regards the energy of its electrons. Thus, the orbit with quantum number 1 is the first; that of quantum number 3 is the third; and an electron in passing from the level of quantum number 1 to that of quantum number 3 must gain energy corresponding to the difference in energy between the two levels.

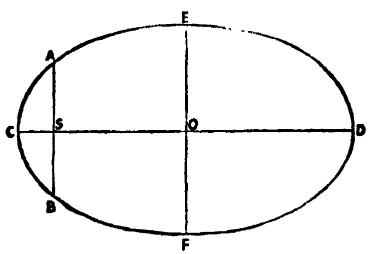

FIG. 43.—Ellipse showing axes, focus and latus rectum.
Major axis = CD; minor axis = EF.
Focus = S; latus rectum = AB.

But the question is not quite so simple as this. It is known that in the majority of cases the orbits are not circular, but are elliptical (to a close approximation), with the nucleus at one focus.

Sommerfeld pointed out also, that if the orbit is elliptical, the electron must approach nearer the nucleus at some part of its travel than at others, and will therefore move quicker at the place of nearer approach. This must cause its mass to increase, for on the principle of relativity, the mass of an electron depends on its speed, and becomes infinite when the speed is that of light. This means that instead of keeping to the ellipse, the electron moves a little farther round the nucleus each time, and so the ellipse itself will be rotating all the time. A similar effect is noticed with the planet Mercury, though here the movement of the orbit is very slow.

The motion of the electron thus consists of two motions superimposed on each other. The one is the elliptical motion of the electron, and the other the rotation of the ellipse itself about the nucleus. We must apply the quantum theory to both motions. If we quantise the actual orbit, we must also quantise its rotation.

As a result of this quantisation, the electrons will be able to travel only in orbits of definite eccentricity. There are thus two quantum numbers required to specify an orbit, one of these is given the symbol n, and is called the principal quantum number, the other is k, and is called the subsidiary or azimuthal quantum number. It can be shown that the principal quantum number n determines the major axis of the ellipse, so that all the orbits for the same n have the same major axis. The second quantum number, k, is connected with n by the relationship

$$\frac{\text{length of major axis}}{\text{length of latus rectum}} = \frac{n^2}{k^2}.$$

It is also true to say that

$$\frac{\text{length of major axis}}{\text{length of minor axis}} = \frac{n}{k}.$$

Thus, if n is 4 and k is 1, the orbit will be an ellipse for which the

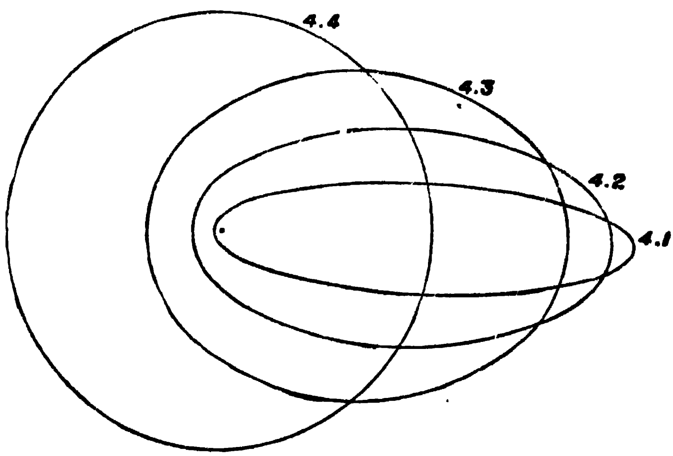

FIG. 44.—Orbits of principal quantum number 4. (From Andrade, *Structure of the Atom*, by permission of Messrs. G. Bell & Sons.)

ratio of the major to the minor axis is 4. It is clear that whilst k can have any integral value up to n, it cannot exceed n. When k becomes equal to n, the orbit is circular. For orbits of principal quantum number 4, there are four elliptical orbits (including the circle as a limiting case). They are the 4_1 level, in which the ratio of the major to the minor axis is 4; the 4_2 level, in which this ratio is 2, the major axis having the same length as in the 4_1 orbit; the 4_3 level, in which the ratio is 4 to 3; and the 4_4 level—a circle. These orbits are shown in Fig. 44.

The possible electronic orbits for hydrogen, up to the principal

quantum number 4, are shown in Fig. 45. In the ordinary condition the electron would be in the 1_1 orbit, but if the atom is excited, *i.e.*, if it has taken up energy and the electron has been displaced to some outer orbit, it may be in the orbit of quantum number 2, 3 or 4, or even higher.

What information concerning these two quantum numbers, the principal and the azimuthal, can be derived from spectra? We may consider for this purpose the spectra of the alkali metals lithium, sodium and potassium. Since both these atoms are regarded as having one electron in some distinct orbit, imparting to them the property of univalency (§ 59), we have transitions which affect only one electron (as regards optical spectra), and the spectra may

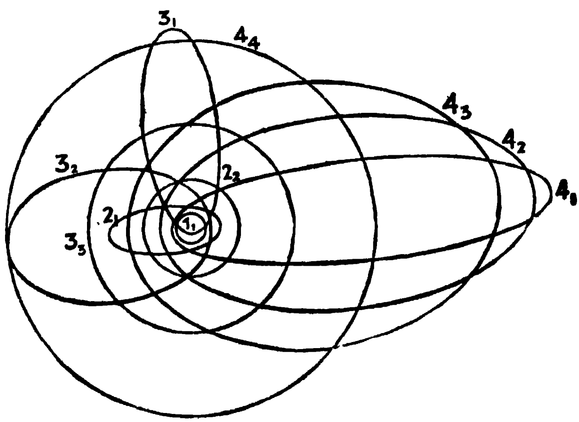

Fig. 45.—Electronic Orbits in the excited Hydrogen Atom. (Adapted from H. S. Taylor, "*A Treatise on Physical Chemistry*," Fig. 11, p. 1093, by permission of Messrs. Macmillan & Co. Ltd.)

therefore be compared with the hydrogen spectrum. But, in the case of the alkali metals, there is an inner ring of electrons. If the orbit of the outer electron is quite distinct from the others, the atom may be expected to give a spectrum like that of hydrogen, but if the orbit of the outer electron interpenetrates the inner orbits, the electron may be considerably deviated from its path by the effect of the nucleus, and so the magnitude of the term which corresponds to its energy level will be quite different from that of hydrogen.

Now the hydrogen terms are given, as we have seen (§ 50), by the expression

$$\nu_0 = \frac{R}{n^2}.$$

Hence the quantum number for an alkali metal should be given by

$$n_{eff} = \sqrt{R\nu_0}.$$

This is called the effective quantum number, and can be calculated from the known values of R and ν_0, obtained from the spectra of the atoms. The values of the effective quantum numbers for the levels giving rise to the S, P, D and F spectra are given in the Table, together with the values of the actual quantum number.

TABLE XX.—EFFECTIVE QUANTUM NUMBERS OF FIRST TERMS

Element.	Spectrum.	n_{eff}	n	k
Lithium . .	S	1·59	2	1
	P	1·96	2	2
	D	3·00	3	3
	F	4·00	4	4
Sodium . .	S	1·63	3	1
	P	2·12	3	2
	D	2·99	3	3
	F	4·00	4	4
Potassium .	S	1·77	4	1
	P	2·23	4	2
	D	2·85	3	3
	F	3·99	4	4

In the case of the D and F spectra there is practically no difference in the values of the numbers. We argue from this that here there is no appreciable perturbing effect due to the nucleus, and hence the orbits do not approach the nucleus. But when we consider the P and S terms we find that the numbers differ considerably, and so these orbits are not closely related to the orbits in the hydrogen atom. They must have marked eccentricity. The S levels are therefore supposed to be the most eccentric, and they are given the azimuthal quantum number 1. It has been shown that the values of k associated with the orbits giving rise to the S, P, D, F levels are 1, 2 and 4 respectively. We thus have an explanation of the differences shown in the various spectral series S, P, D, F (§ 48).

If only one electron is concerned in the production of the spectral lines of an element, the above method gives valuable information concerning its orbit. It has already been seen that the largest numerical term corresponds to the normal state of the atom (§ 50). If it is possible to find the sequence to which the largest term of the spectrum of an atom belongs, it is clear that this will give the eccentricity of the orbit of the electron which has been last added

(the "optical" electron) in making up the element, and which will be the one removed on ionisation. Thus, in forming an element from the one preceding it in the Periodic Table, one electron must be added (and, of course, a corresponding change in the nucleus must occur, but we are not concerned with that at present). This electron will be the one which will split off again when the atom is ionised, and it will be removed to infinity. The term corresponding to this is the largest numerical term. If this is a P term, then the "optical" electron must be in an orbit for which $k = 2$. If it is an S term, the value of k is 1.

Thus, the largest term for sodium is of the S type, as is also that of magnesium, so that the last electron to be added in the making of these atoms from the previous atom in the Periodic Table must go in the 3_1 orbit. With aluminium, however, the largest term is a P term, so that the added electron goes in the 3_2 orbit. Potassium and calcium give normal terms of the S type. The added electron is in the 4_1 orbit. Scandium is the first element in which the largest term is of the D type, so that the azimuthal quantum number for the last electron to be added in making this atom is 3. If we write out the structure of the elements we have considered above, putting down the number of electrons in each orbit, we have :—

TABLE XXI

Energy levels, n_k	1_1	2_1	2_2	3_1	3_2	3_3	4_1
K	2	2	6	2	6	—	1
Ca	2	2	6	2	6	—	2
Sc	2	2	6	2	6	1	2

The way in which the n levels are decided will be clear after reading the next section.

This principle is of the greatest use in deciding the orbits of electrons in the atom, but it is not, however, universally applicable. It has been derived on the assumption that only one electron is involved in the production of the lines, whereas with the heavier elements there is no doubt that this is no longer true.

53. Arrangement of Electrons in Orbits.—The question must first be settled as to how many electrons can form one level, and then how these levels are related to each other.

In answer to the first point we may say that the number of electrons which can complete an energy level is not the same for all the levels. It is known that the size of a stable group of electrons is of the form $2n^2$, and may thus contain 2, 8, 18 or 32 electrons according as n is 1, 2, 3 or 4. The successive periods in the Periodic Table are due to this fact

Let us consider the general properties of the elements in the arrangement of the Periodic Table. We have first the elements hydrogen and helium. The first has one, the second two, electrons, so that in helium we have the first stable grouping completed. Next follow the eight elements from lithium to fluorine, after which is the inert-gas neon. It may be inferred that in these elements the next stable grouping is gradually filling up. The second short series from sodium to chlorine has a very similar gradation of properties to the first short series, and we therefore have no reason to believe that the addition of electrons to the stable configuration of the inert gases as we proceed along the series takes place in any different way in these two series. Next comes argon, which is followed by a series of eighteen elements up to krypton. Starting with potassium and calcium, the first part of the series shows a similar gradation of properties as is found in the short periods already mentioned, although the resemblance between these elements and those of the preceding short series begins to fall off with scandium and titanium. Thus there is far less resemblance between, say, sulphur and chromium, than between magnesium and calcium. Moreover, when we get to the eighth place, where an inert gas might be expected to make its appearance, we find its place occupied with three closely related elements—iron, nickel and cobalt. Then follow the elements from copper to krypton, which show, in general, a similar gradation of properties to those already noted in the short periods.

The same behaviour is found in the next period, which again consists of eighteen elements, and contains a triad, which takes the place of an inert gas.

The next period is a very long one, containing thirty-two elements, amongst them the rare earths, which have been a problem as regards the Periodic System. We have here fourteen elements (from cerium to lutecium), all very closely related, and all tervalent. The elements following them, viz., hafnium to platinum, are very similar to the middle elements of the previous long groups. These are followed by a short period of eight, like the first two short periods, and then by a few elements which do not make up a group.

Consideration of these points enables us to see how the electrons are arranged in levels in these elements without, however, allowing us to state exactly the *n* and *k* numbers of the orbits.

It is clear that in the first two short periods the addition of electrons takes place in similar ways, as has already been pointed out. We must assume that the first quantum group is filled in helium, that in lithium one electron is added in the second quantum group, and that the addition of electrons to this group takes place progressively

as we go through the successive elements in the Periodic Table until we get to neon, the next inert gas, in which this group has become complete. Now electrons are added progressively to the third quantum group until it becomes complete in argon, and the atoms in the first short group exhibit a gradation of properties similar to those in the second short period because the electrons are added similarly, but form an orbit with a quántum number 3 instead of 2.

Coming to the first long series, the first element is potassium, which has one electron more than the stable arrangement found in argon. This electron is in the 4_1 orbit. Similarly, calcium has one more than potassium, and this is also in the 4-quantum orbit. With scandium, however, the additional electron goes into the 3-quantum orbit, leaving still two electrons in the 4-quantum orbit. The

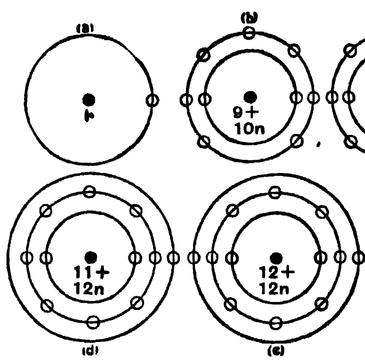

Fig. 46.—The atomic models (simplified) of (*a*) hydrogen, (*b*) fluorine, (*c*) neon, (*d*) sodium, (*e*) magnesium. The second quantum group is completed in neon; in sodium and magnesium the additional electrons have entered the third group.

number of electrons in the latter orbit now remains constant until we get to chromium, the 3-quantum orbit filling up in the meantime. With chromium, one of the 4-quantum electrons is pulled into the 3-quantum orbit. But after this, the 3-quantum orbit fills up to 18. This explains the fact, previously noted, that with scandium a new type of element is being made, for the properties of the elements from scandium to nickel differ from those in the preceding short series much more than would be expected if their formation proceeded on normal lines. These elements, from scandium to nickel, in which the third quantum group is filling up, are called the transition elements. The filling up of this group accounts in a very satisfactory manner for the existence of the long period, and of ten elements in the first row of it. The structure of the inert gas krypton is then (2, 8, 18, 8). Notice that the group of eighteen

electrons does not occupy the outermost position. In every case, the inert gas structure finishes with a complete ring of eight electrons.

The second long period is built up in a similar way, so that xenon is not (2, 8, 8, 18, 18), but (2, 8, 18, 18, 8). In the next period we have a large group containing thirty-two electrons in the middle, the gas radon being (2, 8, 18, 32, 18, 8).

In this period, the first element, cæsium, has one electron in the 6_1 orbit, followed by barium with two in that orbit. Next we have lanthanum, which starts a set of transition elements, the 5_3 orbits filling up; but with the next element, cerium, the 4-quantum group not yet complete, claims the newly added electron. This begins the series of rare-earth elements, fourteen in number. For the thirteen elements after cerium, the added electrons go into the 4_4 orbits, until this is complete, after which the 5_3 orbit takes them, continuing the transition elements down to platinum. After this the 6-quantum orbits begin to fill up, and the series finishes with radon, with a structure (2, 8, 18, 32, 18, 8).

With the next, but incomplete series, a similar behaviour is noticed, a set of transition elements starting with actinium.

These facts are set out in the Table given below.

TABLE XXII

Quantum group, n		1	2	3	4	5
He	2	2	—	—	—	—
Ne	10	2	8	—	—	—
A	18	2	8	8	—	—
Kr	36	2	8	18	8	—
Xe	54	2	8	18	18	8
Ra-Em or Rd.	86	2	8	18	32	18

Although we have derived these relationships by considering the general chemical properties of the elements, it is possible to derive them physically, as was done by Bohr. It is to be noted that the maximum number of electrons that a group can hold is $2n^2$, where n is the principal quantum number, but that even though a group may contain eighteen or thirty-two electrons, a position of comparative stability is reached when there are only eight electrons in the group. Thus argon is a very stable gas, and has a stable arrangement of electrons although it only contains eight in the third quantum orbit, a level which is capable of holding eighteen. The outer orbit of an inert gas always contains eight electrons, the middle orbits taking a larger number of electrons.

We have referred these orbits to their principal quantum number n, but there is still the question of the eccentricity of the elliptical

TABLE XXIII.—ATOMIC STRUCTURES

n		1	2			3					4						
	k_j	1_1	1_1	2_1	2_2	1_1	2_1	2_2	3_2	3_3	1_1	2_1	2_2	3_2	3_3	4_3	4_4
1	H	1															
2	He	2															
3	Li	2	1														
4	Be	2	2														
5	B	2	2	1													
6	C	2	2	2													
7	N	2	2	3													
8	O	2	2	4													
9	F	2	2	5													
10	Ne	2	2	2	4												
11	Na	2	2	2	4	1											
12	Mg	2	2	2	4	2											
13	Al	2	2	2	4	2	1										
14	Si	2	2	2	4	2	2										
15	P	2	2	2	4	2	3										
16	S	2	2	2	4	2	4										
17	Cl	2	2	2	4	2	5										
18	A	2	2	2	4	2	2	4									
19	K	2	2	2	4	2	2	4			1						
20	Ca	2	2	2	4	2	2	4			2						
21	Sc	2	2	2	4	2	2	4	1		2						
22	Ti	2	2	2	4	2	2	4	2		2						
23	V	2	2	2	4	2	2	4	3		2						
24	Cr	2	2	2	4	2	2	4	5		1						
25	Mn	2	2	2	4	2	2	4	5		2						
26	Fe	2	2	2	4	2	2	4	6		2						
27	Co	2	2	2	4	2	2	4	7		2						
28	Ni	2	2	2	4	2	2	4	8		2						
29	Cu	2	2	2	4	2	2	4	4	6	1						
30	Zn	2	2	2	4	2	2	4	4	6	2						
31	Ga	2	2	2	4	2	2	4	4	6	2	1					
32	Ge	2	2	2	4	2	2	4	4	6	2	2					
33	As	2	2	2	4	2	2	4	4	6	2	3					
34	Se	2	2	2	4	2	2	4	4	6	2	4					
35	Br	2	2	2	4	2	2	4	4	6	2	5					
36	Kr	2	2	2	4	2	2	4	4	6	2	2	4				

orbits to be considered, *i.e.*, the number of electrons in the different k levels for each quantum number must be obtained.

It may be stated here that as a result of work on the multiplets observed in the spectra of atoms it has been found necessary to

	n / kj	1	2	3	4: 1_1	2_1	2_2	3_2	3_3	4_3	4_4	5: 1_1	2_1	2_2	3_2	3_3	6: 1_1
		—	—	—													
37	Rb	2	8	18	2	2	4					1					
38	Sr	2	8	18	2	2	4					2					
39	Y	2	8	18	2	2	4	1				2					
40	Zr	2	8	18	2	2	4	2				2					
41	Nb	2	8	18	2	2	4	4				1					
42	Mo	2	8	18	2	2	4	5				1					
43	Ma	2	8	18	2	2	4	5				2					
44	Ru	2	8	18	2	2	4	7				1					
45	Rh	2	8	18	2	2	4	8				1					
46	Pd	2	8	18	2	2	4	4	6			–					
47	Ag	2	8	18	2	2	4	4	6			1					
48	Cd	2	8	18	2	2	4	4	6			2					
49	In	2	8	18	2	2	4	4	6			2	1				
50	Sn	2	8	18	2	2	4	4	6			2	2				
51	Sb	2	8	18	2	2	4	4	6			2	3				
52	Te	2	8	18	2	2	4	4	6			2	4				
53	I	2	8	18	2	2	4	4	6			2	5				
54	X	2	8	18	2	2	4	4	6			2	2	4			
55	Cs	2	8	18	2	2	4	4	6			2	2	4			1
56	Ba	2	8	18	2	2	4	4	6			2	2	4			2
57	La	2	8	18	2	2	4	4	6			2	2	4	1		2
58	Ce	2	8	18	2	2	4	4	6	1		2	2	4	1		2
59	Pr	2	8	18	2	2	4	4	6	2		2	2	4	1		2
60	Nd	2	8	18	2	2	4	4	6	3		2	2	4	1		2
61	Il	2	8	18	2	2	4	4	6	4		2	2	4	1		2
62	Sm	2	8	18	2	2	4	4	6	5		2	2	4	1		2
63	Eu	2	8	18	2	2	4	4	6	6		2	2	4	1		2
64	Gd	2	8	18	2	2	4	4	6	7		2	2	4	1		2
65	Tb	2	8	18	2	2	4	4	6	8		2	2	4	1		2
66	Ds	2	8	18	2	2	4	4	6	9		2	2	4	1		2
67	Ho	2	8	18	2	2	4	4	6	10		2	2	4	1		2
68	Er	2	8	18	2	2	4	4	6	11		2	2	4	1		2
69	Tm	2	8	18	2	2	4	4	6	12		2	2	4	1		2
70	Yb	2	8	18	2	2	4	4	6	13		2	2	4	1		2
71	Lu	2	8	18	2	2	4	4	6	6	8	2	2	4	1		2
72	Hf	2	8	18	2	2	4	4	6	6	8	2	2	4	2		2
73	Ta	2	8	18	2	2	4	4	6	6	8	2	2	4	3		2
74	W	2	8	18	2	2	4	4	6	6	8	2	2	4	4		2

introduce still further modifications to the orbits, requiring another quantum number j, which may represent the direction of spin of the electron round its own axis.[1] It is called the inner quantum

[1] The quantum number j is the vector sum of the two quantum numbers l and s. On the new quantum mechanics $l = k - 1$, and $s = \frac{1}{2}$. $s\frac{h}{2\pi}$ is the angular momentum of the electron spin. For a one electron system $j = l \pm \frac{1}{2}$

n / *kj*		1	2	3	4	5 1_1	2_1	2_2	3_2	3_3	6 1_1	2_1	2_2	3_2	3_3	7 1_1
75	Re	2	8	18	32	2	2	4	5		2					
76	Os	2	8	18	32	2	2	4	7		1					
77	Ir	2	8	18	32	2	2	4	9		2					
78	Pt	2	8	18	32	2	2	4	10		2					
79	Au	2	8	18	32	2	2	4	4	6	1					
80	Hg	2	8	18	32	2	2	4	4	6	2					
81	Tl	2	8	18	32	2	2	4	4	6	2	1				
82	Pb	2	8	18	32	2	2	4	4	6	2	2				
83	Bi	2	8	18	32	2	2	4	4	6	2	3				
84	Po	2	8	18	32	2	2	4	4	6	2	4				
85	—	2	8	18	32	2	2	4	4	6	2	5				
86	Rd	2	8	18	32	2	2	4	4	6	2	2	4			
87	—	2	8	18	32	2	2	4	4	6	2	2	4			1
88	Ra	2	8	18	32	2	2	4	4	6	2	2	4			2
89	Ac	2	8	18	32	2	2	4	4	6	2	2	4	1		2
90	Th	2	8	18	32	2	2	4	4	6	2	2	4	2		2
91	Pa	2	8	18	32	2	2	4	4	6	2	2	4	3		2
92	U	2	8	18	32	2	2	4	4	6	2	2	4	4		2

number, and besides explaining the hyperfine structure of spectra, it governs the behaviour of the lines of the spectrum in a magnetic field. By the application of various relationships that have been discovered, a discussion of which is beyond the scope of this book, the values of *k* and *j* for most elements have been satisfactorily settled.

We can now sum up our picture of the atom. It consists of a nucleus which has a resultant positive charge equal to the charge on the electrons which travel in orbits outside it. These orbits are approximately elliptical, but themselves are precessing. The orbits are defined by the possession of certain amounts of energy and no other, so that the number of orbits is limited. The orbits may interpenetrate. The electrons themselves in these orbits are spinning.

The arrangements of electrons in the various atoms are given in the Table above.

54. The Nucleus.—A fairly complete picture of the arrangement of the extra-nuclear electrons in the atom has now been presented. These planetary electrons are of importance to us as chemists. The nature of the nucleus is not quite so important, as it does not affect the chemical properties of the atom to anything like the extent the extra-nuclear electrons do. The study of the nucleus is of con

siderably greater difficulty than that of the exterior of the atom and it is only within recent years that any knowledge of its nature has become available.

It is largely owing to the work of Rutherford and of Gamow that our knowledge of the arrangement of the ultimate particles in the nucleus has advanced. It would appear that the α-particle is moving in the nucleus in a quantised orbit, because it is always liberated with a constant velocity. That α-particles do occur in the nucleus is shown by radioactivity, which has already been discussed. The α-particle is a positively charged helium atom, and contains therefore two protons and two neutrons.

Estimates of the size of the nucleus have been derived from two sources. The scattering of α-particles leads to the view that the radius of the nucleus of a heavy atom is less than $3{\cdot}2 \times 10^{-12}$ cm., but radioactivity leads to a value of about $6{\cdot}5 \times 10^{-12}$ cm. The difficulty is to reconcile these two estimates. This can be done if we assume that if any particles of the nucleus do extend to such a distance as 6×10^{-12} cm., they must be electrically neutral. These neutral particles may be the neutrons already referred to in Chapter II. (§ 42).

It is now generally considered that there are three regions in the nucleus. The central part consists of a tightly packed arrangement of neutrons and protons, and has a radius of about 1×10^{-12} cm. This central part of the nucleus is probably common to several elements, additions to the nucleus occurring to the outer parts. It is certainly common to radioactive elements. After this is a region occupied by neutrons and positive nuclei of small mass, moving with a velocity approaching that of light. These extend to a radius of about $1{\cdot}5 \times 10^{-12}$ cm. The outer region contains neutral particles.

55. Electron and Nuclear Spin.—When the Bohr theory was applied to atoms containing more than one planetary electron, it was found that the three quantum numbers, n, k, j, already mentioned, were insufficient to describe accurately the spectral, and other properties of the atom. New quantum numbers were therefore introduced, thus making the theory considerably more complicated. These new numbers were supposed to stand for nuclear spin, and other properties. It is doubtful, however, whether any physical significance should be attached to these numbers. They are useful in the mathematical theory, but may have no simple physical meaning.

The *Pauli Exclusion Principle*, which states that no two electrons in an atom may possess completely identical sets of quantum numbers, has proved of service in deciding the quantum numbers to be assigned to any electron.

Although the quantum numbers themselves may not directly represent electron and nuclear spin, there is no doubt that these spins exist. It has been shown, by a method outside the scope of this book, that the multiplicity of spectral lines (§ 49) may be explained by assuming the existence of electron spin. Elements with an even atomic number have been found to give lines with an odd multiplicity (singlets, triplets, quintuplets, etc.), whereas elements with an odd atomic number give lines with an even multiplicity (doublets, quartets, sextets, etc.).

The spin-quantum numbers have been used by Heitler and London in their quantum theory of covalent linkages (§ 60).

56. Wave Mechanics.—Although Bohr's theory is able to explain in a very satisfactory manner the periodicity running through the properties of the elements, the presence of transition groups in the Periodic System, and many other points connected with the nature of the atom, it fails to answer completely more complicated questions which arise.

For example, Bohr's quantum theory of the atom gives no explanation of the intensities of spectral lines unless further assumptions are made. Nor can it explain the more complicated spectra. Even the spectrum of helium, next in difficulty to that of hydrogen, cannot be adequately dealt with by the quantum theory. Moreover, the arbitrary postulates on which it is based, running, as they do, completely counter to classical conceptions, are difficult to accept without explanation.

The system of wave-mechanics provides an explanation of the Bohr postulates, and at the same time extends the theory so that the more complicated problems of atomic structure can be effectively attacked.

Bohr's theory looks upon the electron as a material particle, but in 1924 de Broglie put forward the new idea that all moving material particles of whatever nature have wave-properties associated with them. These particles will, of course, include electrons. The fact that electrons can possess the properties both of corpuscles and waves was suggested by the similar state of affairs existing with light. As is well known, Newton's view of the nature of light was that it was corpuscular.[1] His theory accounted satisfactorily for the laws of reflection and some other properties of light. In the nineteenth century, however, Young's experiments on interference and diffraction of light led to the view that light possessed the properties of waves, a theory put forward as early as 1690 by

[1] Newton does, however, appear to have introduced a periodicity into his theory to explain, for example, Newton's rings. To this extent he may be said to have anticipated the particle-wave-motion theory.

Huygens, but discarded owing to the greater prestige of Newton. Young's work caused the complete destruction, for the time being, of the corpuscular theory, and it was shown that the wave theory could not only explain the newly discovered phenomena of interference, but also the laws of reflection and refraction in a manner just as satisfactory as the corpuscular theory. Early in the present century, however, new phenomena were discovered which the wave theory by itself could not explain. The photo-effect and the Zeeman effect demanded that light should be regarded as made up of photons, which possessed the properties of both corpuscles and waves. Photons were looked upon as "wave packets" or pulses, and were associated with energy proportioned to the frequency of the wave—quanta, in fact, given by Planck's equation

$$E = h\nu.$$

The application of a similar conception to moving material particles is the basis of wave-mechanics. De Broglie supposed that the wave-length, λ, associated with a moving particle is given by

$$\lambda = h/mv,$$

where h is Planck's constant, m is the mass, and v the velocity of the moving particle.

If this is the case, it should be possible to calculate the wave-length associated with the electron when it is moving with a given velocity. When this calculation is carried out the wave-length associated with an electron which has acquired energy by falling through a potential difference of 100 volts is found to be 1·22 Å, which is of the order of the wave-length of soft X-rays.

If electrons are, in fact, associated with waves it would be expected that they would show the phenomena of interference and diffraction in the same way as light. This suggestion, which was made by Elsasser in 1925, was verified by Davisson and Germer, who showed experimentally that there was selective reflection of electrons at the surface of a nickel crystal. The results were very similar to those obtained with X-rays, and when the effective wave-lengths of the electrons were calculated by the usual diffraction formula the values obtained agreed with those given by the de Broglie equation within the limits of experimental error. These experiments, and those of G. P. Thomson, are referred to again in § 130.

Perhaps the most outstanding experimental evidence that electrons are associated with waves is provided by the fact that it is possible to construct an electron microscope. It is well known that the resolving power of an optical microscope is limited by the wave-

length of the light used, the size of the object which can be successfully seen varying with the wave-length. The lowest wave-length that can be used with an optical microscope is in the neighbourhood of 3000 Å. Since electrons can be deflected by electric and magnetic fields it is possible to construct magnetic and electrostatic focusing systems and hence to use a beam of electrons in the same way as a beam of light. Of course, the electrons cannot be "seen" in the same way as light, but they can be photographed, like X-rays. The smallest object that can be "seen" with an optical microscope has a diameter of about 2×10^{-4} cm., but since electrons have a very much smaller effective wave-length, the electron microscope can be used to "see" objects of diameter as small as 10^{-6} cm., which is almost of molecular dimensions. With the aid of this instrument it has been possible to photograph macro-molecules, such as protein molecules. The disadvantage of the electron microscope lies in the fact that the beam of electrons may destroy, or damage the object being "viewed," particularly biological material.

56a. The Dual Nature of Matter and Waves.—It has thus been established experimentally that electrons have the properties of waves. At the same time they have the properties of particles, since they have mass and momentum, which can only be thought of as the attributes of corpuscles.

Not only is this true of the electron, but it also holds for atoms and molecules. Stern showed in 1932 that atomic and molecular rays were diffracted at crystal surfaces in the same way as electrons, so that we are forced to the conclusion that all matter has a wave aspect as well as a particle aspect. Thus both matter and electromagnetic waves have a dual nature. Matter has a wave aspect, and waves have a particle aspect. The two are complementary. It can be shown that if an experiment is devised to test the wave-properties of matter, then the matter behaves entirely as waves. Conversely if an experiment is devised, say, to measure the momentum of a particle, then the material side of matter only will be in evidence. If we consider wave-length λ, as the property of waves we are thinking of, and momentum as the property of particles, the two are connected by the de Broglie equation

$$\lambda = \frac{h}{mv}$$

since mv is the momentum. Thus the connecting factor is h, Planck's constant.

The de Broglie equation can also be used to connect frequency ν

with energy ($\frac{1}{2}mv^2$) since the wave-length, $\lambda = \frac{v}{\nu}$. We thus have

$$\frac{mv^2}{h} = \frac{\frac{1}{2}mv^2}{h}.$$

We see again that the factor connecting frequency (a wave property) with kinetic energy (a particle property) is Planck's constant, h.

The system of wave-mechanics attempts to explain this dual nature. Schroedinger at first supposed electrons to be wave-packets, but although the formulæ deduced on this basis are correct, this interpretation cannot be supported since wave-packets would, in course of time, be dissipated. This difficulty can be avoided by supposing that the wave-packet is carried on a guiding wave. An analogy may be useful. The guiding wave may be compared with the carrier wave in wireless transmission. In wireless, waves of a certain wave-length are transmitted from the station, and these are constant in length, but superimposed upon them is another wave-motion, which ultimately translates itself into the sound we hear in the loud speaker. This corresponds to the wave-packet.

The guiding wave is given by the Schroedinger equation

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(W - V)\psi = 0$$

where W is the total energy and V the potential energy of the particle

The amplitude ψ of this guiding wave at any point is the square root of the probability that an electron is to be found at that point. If the amplitude is zero the probability of finding the electron at that place is negligibly small. If the equation is solved for the special boundary conditions which are imposed by the physical nature of the question, *viz.*, that ψ and $\dot{\psi}$ are everywhere single-valued, continuous, and finite, certain values of W are found. The Schroedinger equation can, in fact, only be solved under these conditions, when $W = \frac{2\pi^2 \ \varepsilon Z^2}{n^2 h^2}$ where n is any integer. For any other value of n the waves interfere with each other and are destroyed.

The Schroedinger equation thus leads to the same numerical result as the Bohr theory, but without the use of the arbitrary assumptions made by Bohr.

56b. Probability in the Theory of Atomic Structure.—It will be seen that in the Schroedinger equation the probability of the electron being in a certain element of volume is an important aspect of the theory. In fact it is now held that the *exact* position of an electron cannot be determined if at the same time we require to

know its *exact* velocity. This is expressed in Heisenberg's uncertainty principle, which states that it is impossible to determine simultaneously both the momentum and the position of a particle accurately.

Heisenberg showed that if Δx is the uncertainty in determining the exact position of a particle within the wave-packet, and Δp is the uncertainty in determining the momentum, $\Delta x \, . \, \Delta p$ is approximately equal to Planck's constant h.

This means that the law of causation can no longer be regarded as the basis of physics. Instead, probability is the guiding principle. We cannot say that an electron is moving in a certain orbit; we can only say that the probability of its being there is very great, but there is always the chance that it may be elsewhere. This leads further to the view that nothing is impossible. What classical mechanics would lay down as impossible, as, for example, a body rising from the table on which it is placed, against the action of gravity, can now only be said to be highly improbable. The philosophical consequences of this view of matter are very important and far-reaching, but they cannot be discussed here.

For a fuller treatment of wave mechanics and its application to problems of atomic structure and other properties of matter, where it has completely displaced the Bohr theory, the reader should consult one of the specialised texts mentioned at the end of this chapter.

57. Ortho- and Para-Hydrogen.—The prediction that there should be two forms of hydrogen, which was made on the basis of the wave-mechanics, is interesting, as it has been verified experimentally.

The nucleus of the atom is spinning, and when two hydrogen atoms come together to form a molecule, they may unite in such a way that the nuclear spins aid each other (symmetrical) or neutralise each other (anti-symmetrical) In the first instance, ortho-hydrogen is produced, and in the latter, para-hydrogen. The ordinary gas consists of a mixture of the two forms in the proportion of about three parts of ortho- to one part of para-hydrogen, at ordinary temperatures. The proportions of the two forms present vary with the temperature. Since the form with no resultant spin, *i.e.*, the para-form, will have less energy than the other, the gas should consist mainly of this form at very low temperatures. This was tested by Bonhoeffer, who was able to prepare 99·7 per cent. pure para-hydrogen by cooling. In consequence of the difference in energy content, the two forms will possess different specific heats (Chapter VII., §§ 131, 139).

SUMMARY

In order to give a theoretical explanation for black-body radiation, Max Planck supposed that energy was not emitted or absorbed by a vibrating body continuously, but in quanta, of magnitude $h\nu$, where ν is the frequency of the radiation, and h a universal constant, known as Planck's constant.

Bohr showed that the Rutherford atomic model was unstable, and, if it were accurate, would indicate that the spectra of elements in the form of gas should be continuous, whereas they are line-spectra. He applied quantum considerations to the motion of the electrons, supposing (1) that the electrons moved only in certain orbits, in which they radiated no energy. These were called "stationary states." The electrons in these states possess certain definite energies, the values of which are restricted by certain rules of quantising. (2) When an electron passes from an orbit of energy E_1 to another of energy E_2, monochromatic radiation is emitted or absorbed, the relationship governing the frequency, ν, of this radiation being $E_1 - E_2 = h\nu$. This theory gives a satisfactory explanation of atomic spectra, and particularly of the hydrogen spectrum. It is possible to calculate the number of electrons in each orbit in any atom, and the results agree in a remarkable way with conclusions based on the Periodic Table.

The Bohr theory is now comprised in the new Quantum- and Wave-Mechanics.

SUGGESTIONS FOR FURTHER READING

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QUESTIONS

(1) Describe the evidence afforded by a study of spectra concerning the nature of the atom.

(2) Show how the various line series in the hydrogen spectrum have been explained.

(3) Upon what principles is it possible to discover the orbits of the electrons outside the nucleus?

(4) Give some account of the recent work on the structure of the nucleus.

CHAPTER IV

VALENCY

58. Development of the Theory of Valency.—Such radical changes have taken place in our views of the meaning of valency that it is advantageous to trace the development of the conception.

Like many other theories, the theory of valency arose from the application of the atomic theory to chemical behaviour. The burning question at the beginning of the nineteenth century was the way in which atoms combined with each other. From a study of electrolysis, Davy, in 1807, came to the conclusion that opposite parts of the atom (defined according to the view of Dalton, which included atoms of both elements and compounds) possessed opposite electrical charges, produced by induction. His view does not seem to have been generally accepted, or to have been given serious thought. A few years later, in 1812, Berzelius put forward an hypothesis which was considerably more comprehensive. Berzelius started with the assumption that each atom possessed a characteristic electrical polarity, which was concentrated in at least two poles, of different intensity and different sign. Only the resultant electric force mattered as regards external properties, so that although an atom might possess numerous different charges, it appeared to be unipolar. Compounds were formed by complete, or only partial neutralisation of the opposite charges of other atoms. Thus, according to this view, all compounds were made up of two parts, electrically opposite in character, and the theory was therefore called the dualistic theory.

Thus the iron atom was supposed to have a positive charge, and the oxygen atom a negative one, and combination occurred by the partial neutralisation of these charges,

$$\overset{+}{\mathrm{Fe}} + \overset{-}{\mathrm{O}} = \overset{+}{\mathrm{Fe}}\mathrm{O}.$$

Similarly sulphur had a positive charge which was fairly large, and could take up three atoms of oxygen.

$$\overset{+}{\mathrm{S}} + 3\overset{-}{\mathrm{O}} = \overset{-}{\mathrm{SO}}_3.$$

The FeO and the SO_3 thus produced were endowed with small residual charges, and could therefore partly neutralise each other and form another compound.

$$\overset{+}{\mathrm{FeO}} + \overset{-}{\mathrm{SO}}_3 = (\mathrm{FeO, SO_3}) = \overset{+}{\mathrm{Fe}}\mathrm{SO}_4.$$

The $FeSO_4$ was still not quite neutral, for it could take up seven molecules of water to make the crystalline salt, $FeSO_4, 7H_2O$.

Berzelius developed this theory almost alone, and some of his assumptions were soon threatened. He had taken oxygen as the most negative element, but the discovery of the properties of chlorine made this questionable. Again, the rising "organic chemistry" did not prove a suitable ground for dualism. At first the organic work received ample explanation at the hands of dualism. Organic compounds were classed together as simple compounds in which groups of atoms, called compound radicals, played the part of elements, an assumption that was put on a firm footing by the work of Gay-Lussac on cyanogen. The radical was the electropositive part of the molecule, which could take up oxygen as the opposite pole. This, of course, naturally excluded the presence of oxygen in compound radicals, and Berzelius had to give in on this point when Liebig and Wöhler discovered the benzoyl radical (C_6H_5CO).

In 1839, Bunsen discovered the radical cacodyl, $C_4H_{12}As_2$. Research on this radical showed in a much clearer way than was hitherto known, how the atoms were combined in it. To this work Berzelius took such a one-sided attitude that he not only lost many of his adherents, but had to face severe attack from many quarters.

5. The discovery of substitution in organic compounds by Dumas was the final point. Dumas showed that the hydrogen in many compounds could be replaced by chlorine, without there being any very great change in the properties of the compound. This is well illustrated by the case of acetic acid. When one atom of the methyl group is replaced by one of chlorine, monochloracetic acid, $CH_2Cl.COOH$, is formed. This substance resembles acetic acid quite closely, and yet the positive hydrogen has been replaced by the very negative chlorine. Facts like this were quite incompatible with dualism, and proved the downfall of the theory.

It may be mentioned in passing that in many respects our modern view of chemical combination resembles the dualistic theory, as will be seen later.

To take the place of the dualistic theory, Dumas proposed a theory of types. This held that the chemical nature of a compound depended primarily on the arrangement and number of its constituent atoms, and that the chemical nature of the atoms was of lesser importance. This theory had advantages, and was improved by Gerhardt in 1856. There were four types on which organic compounds could be classified. These were :—

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}H\\ \\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H\\ \\H\end{matrix}\right\} \qquad \left.\begin{matrix}H\\ \\Cl\end{matrix}\right\}$$

1. Ammonia Type. 2. Water Type. 3. Hydrogen Type. 4. Hydrochloric Acid Type.

Organic compounds were all made by substituting elements or radicals for the hydrogen. Thus, acetamide was of the ammonia type, and was obtained from it by substitution of the acetyl group, C_2H_3O, for one atom of hydrogen. Methyl alcohol was of the water type, since methyl alcohol could theoretically be obtained from water by substitution of a methyl radical for an atom of hydrogen. From these four types, Gerhardt was able, in a most ingenious way, to explain the nature of nearly all the known organic compounds. These views were generally accepted, and the number of types was extended by Williamson and Kekulé. Williamson introduced mixed types, which were derived from two or more of the four types previously mentioned. Thus, benzenesulphonic acid belonged to the mixed type

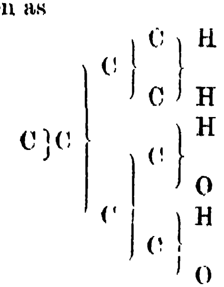
$$\left.\begin{array}{l}H\\H\end{array}\right\} \quad \left.\begin{array}{l}H\\H\end{array}\right\}O \qquad\qquad \left.\begin{array}{l}C_6H_5\\SO_2\end{array}\right\} \quad \left.\begin{array}{l}SO_2\\H\end{array}\right\}O$$

Kekulé introduced the new type—

$$\left.\begin{array}{l}H\\H\\H\\H\end{array}\right\}C$$

methane.

In spite of the existence of these types there was frequently some uncertainty about the type to which a compound belonged, and the accumulation of a large number of types in a complex substance caused confusion. To give an example of the complexity of the explanation, the formula of the radical of phthalic acid may be quoted. This was given as



Before the Gerhardt theory of types had reached the apex of its development, a new point of view was slowly forming. Frankland, in 1852, having studied some organo-metallic compounds, came to the conclusion that the regularities noticed in the composition of organic and inorganic compounds were due to the fundamental properties of the atoms contained in them. The cause of the regu-

larities was due to a *saturation capacity*, which was characteristic of the element, and which could grow within certain limits. The saturation capacity of an element was the number of atoms of another element or radical which could combine with one atom of the original element, to form a compound. For the elements of the nitrogen group, for example, it was three or five. In Frankland's own words : " When the formulæ of inorganic chemical compounds are considered, even the superficial observer is struck with the general symmetry of their constitution ; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements, and it is in these proportions that their affinities are best satisfied ; thus, in the ternal group, we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc., and in the five atom group, NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms." In this way the fundamental basis of the theory of valency was laid.

Kolbe adopted Frankland's idea with enthusiasm, and Kekulé in particular took it up, and arrived at the conception of the quadrivalency of carbon.

Numerous difficulties soon arose. The first question was whether valency was to be regarded as constant, or whether, under certain circumstances, it could vary. Frankland, as has already been stated, believed that it could vary within certain limits, and he was supported in this view by Kolbe. Kekulé, however, defined valency as a fundamental, and strictly invariable property of the atom. However, the fact that valency, or saturation capacity did change, was evident from the existence of such substances as phosphorus trichloride and pentachloride. Both of these are definite compounds, and yet one contains more chlorine than the other. To explain this, Kekulé introduced the system of molecular and atomistic compounds. In atomistic compounds, the elements had their full saturation capacity satisfied. Thus, common salt would be an atomistic compound, because one atom of sodium has combined with one atom of chlorine to make a molecule of sodium chloride, and the valency of the sodium is satisfied. Molecular compounds were made by the combination of two atomistic compounds, in virtue of the forces of affinity. The molecular compounds were supposed to be less stable than the atomistic compounds. Phosphorus trichloride was supposed to be an

atomistic compound. The saturation capacity of the phosphorus had been satisfied by three atoms of chlorine. We should say the valency of phosphorus is three. Phosphorus trichloride, however, can combine with a molecule of chlorine to form phosphorus pentachloride, which, according to Kekulé, was a molecular compound. The valency of phosphorus must still be regarded as three. Phosphorus pentachloride could be written $[PCl_3]Cl_2$, to emphasise this. Moreover, phosphorus pentachloride, on heating, dissociates into phosphorus trichloride and chlorine, and thus it gives all the appearances of being a molecular compound, being less stable than the trichloride, which is atomistic.

However, certain substances, which, according to Kekulé, should be regarded as molecular compounds, were markedly stable. Particularly was this so with phosphorus pentafluoride. The existence of this stable compound convinced many that valency was variable, and militated against Kekulé's theory. Erlenmeyer supposed that each atom had a higher valency limit which need not always be satisfied. In determining valency, the fully saturated compounds only should be considered.

The generally accepted view of valency at this time may be summed up as follows: Every element possesses the power to combine with other elements, but the extent to which this combination can go on is limited. Every element has a saturation capacity. In order to give a definition of saturation capacity, or valency, it may be said that valency is the number of atoms of hydrogen with which one atom of the element will combine. Thus, the valency of oxygen is two, because two atoms of hydrogen combine with one atom of oxygen to form water. The valency of nitrogen is three, because one atom of nitrogen will combine with three atoms of hydrogen to form ammonia, NH_3. Looked at from this point of view, it was natural to assume that atoms possessed valency "bonds," which might be pictured as solid rods extending from the atom. Each "bond" was able to attach itself to one hydrogen atom, which possessed one "bond." Combination, therefore, meant the fusion of these "bonds."

H—O—H

Water. Oxygen has two "bonds": it is bivalent.

```
   H
   |
H—C—H
   |
   H
```

Methane. Carbon has four "bonds": it is quadri-

```
   H
   |
H—N—H
```

Ammonia. Nitrogen has three "bonds"; it is tervalent.

The conception of valency "bonds" made it easier to elucidate chemical combination between elements when one of them was not hydrogen. Many metals would not combine with hydrogen, and so their valencies could not be determined directly according to the above plan. They would, however, combine with chlorine, which was known to be a univalent element, because one atom of chlorine combined with one atom of hydrogen to give one molecule of hydrogen chloride. The valency of the metals could thus be determined through the chloride.

H—Cl	Cl—Ca—Cl
Hydrogen chloride. The chlorine is univalent.	Calcium chloride. The calcium is bivalent because it takes up two univalent chlorine atoms.

Such a view of valency "bonds" would naturally tend to give the idea that valency was a directed force, manifested at certain points in the atom. Erlenmeyer held that this was so, and this view led to the hypothesis put forward by van't Hoff, and almost simultaneously by Le Bel, of space-directed valency forces giving rise in the case of carbon to a tetrahedral model, which, in actual fact, had been suggested by Wollaston some ten years before. The theory of stereochemistry has been of outstanding importance in organic chemistry in explaining the existence of isomers and the phenomenon of optical activity.

Whilst in inorganic chemistry the assumption of variable valency was a necessity, in organic chemistry this was not so, and for a long time the only exception to the quadrivalent carbon atom was found in carbon monoxide, CO. To make carbon always quadrivalent, the theory of double and triple bonds, or unsaturation was suggested. Thus, in ethylene, C_2H_4, it was supposed that the two carbon atoms were linked by two bonds, instead of one,

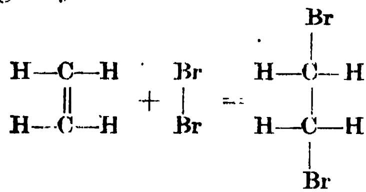
$$\begin{array}{c} H—C—H \\ \| \\ H—C—H \end{array}$$

The bond between the two carbon atoms was called a "double" bond. In acetylene, C_2H_2, it was necessary to suppose that the two carbon atoms were joined by a "triple" bond.

$$\begin{array}{l} C—H \\ ||| \\ C—H \end{array}$$

In both cases the quadrivalency of carbon is preserved. Substances containing these double and triple bonds are said to be "unsaturated." They possess much greater chemical activity than substances containing single bonds only ("saturated" substances), and readily enter into "addition" reactions, whereby they become

saturated. In these, elements or groups are added to the unsaturated molecule without the elimination of any atom. Bromine adds on to ethylene, giving ethylene dibromide.



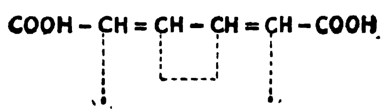
Ethylene. Ethylene dibromide.

The explanation of the additive powers of unsaturated bodies was given in a very satisfactory way by Thiele, who supposed that in the formation of the double bond the affinity force is not completely satisfied, so that part of the valency is left. To this fraction Thiele gave the name "partial valency." These partial valencies were capable of adding on the usual addition elements or groups.

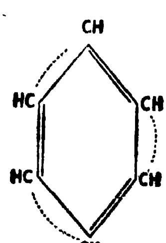
This theory explained in a remarkably neat way the mode of addition of elements to a conjugated system of double bonds, *i.e.*, an alternation of double and single bonds, as found in muconic acid, for example.

$$\underset{}{COOH} - \underset{\delta}{CH} - \underset{\gamma}{CH} - \underset{\beta}{CH} - \underset{\alpha}{CH} - COOH.$$

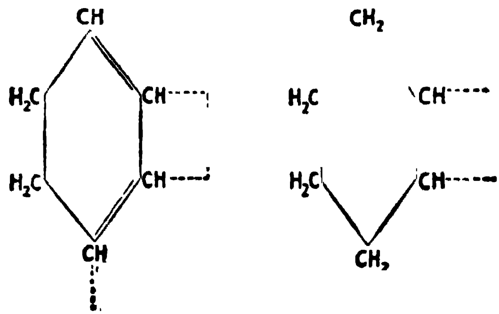
The partial valencies of the β- and γ-CH groups were supposed to satisfy each other, thus :—



This explains the fact that addition to muconic acid always results in the formation of an α-δ-compound. The theory also explains the relative inactivity of benzene, although this substance contains three double bonds. These double bonds form a conjugated system, and so in the end the molecule behaves as if it were saturated.



It also explains the aliphatic nature of the partly hydrogenated ring :—



A consideration of valency in the light of the Periodic Table showed that in the compounds of elements with oxygen, assuming the valency of oxygen to be 2, the valency ascended regularly from Group I. to VII.

Thus, taking the elements in the first short series in order, Table XXIV. shows the compounds formed with hydrogen, and with oxygen.

There were, however, numerous exceptions when other compounds than those with oxygen were considered. Blomstrand pointed out that it was better to take hydrogen compounds. From this point of view, it follows that the valency of an element depends on the nature of the element with which it is compounded. Blomstrand thought this difference to be due to the electrochemical nature of

TABLE XXIV.—VALENCY AND THE PERIODIC TABLE.

	O He	I. Li	II. Be	III. B	IV. C	V. N	VI. O	VII. F
Formulæ of Hydrogen Compounds.	—	LiH	BeX_2**	B_2H_6* B_4H_{10}	CH_4	NH_3	OH_2	FH
Formulæ of Oxygen Compounds.	—	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	— (SO_3)	F_2O* (Mn_2O_7)

* Anomalous.

** Be does not form a hydride, but combines with two atoms of a univalent radical such as (CH_3).

the combining element. He pointed out that a strongly electro-positive or electro-negative element, exerting all its force, always took on the lowest valency. To a certain extent, then, he returned to the view of Berzelius.

Owing to the connection between affinity and valency, many

investigators tried to find an explanation of the former in the hope that it might lead to an elucidation of the latter. However, the view that there was any force behind valency dropped out, and Lothar Meyer summed up the views of the time (1870) by the statement that "By chemical valency we mean the ratio of the atomic weight to the equivalent weight of an element. Valency is thus a pure number." (See Chapter I., § 11.) It is clear, then, that he did not look upon it as any expression of force.

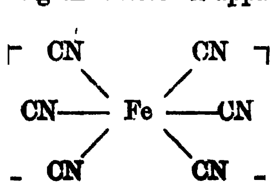
The existence of molecular compounds was still not satisfactorily explained. These compounds included: (1) the so-called double halides, such as the stannichlorides, platinichlorides, silicofluorides, etc.; (2) the complex cyanides (such as ferro- and ferri-cyanides), and nitrites (such as cobaltinitrites); (3) the hydrates; (4) the ammines, complex compounds containing ammonia; and (5) oxonium and sulphonium compounds, etc. (organic compounds of quadrivalent oxygen and sulphur).

The formulæ of some of these compounds are given below :—

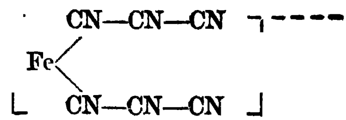
$HAuCl_4$	K_3SbCl_6
Na_3AlF_6	$[(H_2O)_4CrCl_2]Cl$
$(NH_4)_2SnCl_6$	$K_3Co(NO_2)_6$.

These compounds all appear to be made up of two molecules, each of which is capable of a separate existence. Thus, potassium ferrocyanide, $K_4Fe(CN)_6$, may be regarded as compounded of 4KCN and $Fe(CN)_2$. The formula could not, however, be written 4KCN, $Fe(CN)_2$, as this denotes that on solution in water, potassium, ferrous and cyanide ions would be produced, whereas actually, only potassium K^+, and ferrocyanide $Fe(CN)_6^{----}$ ions are produced. Ions, such as the ferrocyanide, ferricyanide, cobaltinitrite, etc., ions, are called complex ions.

The problem is to find some method of writing the formulæ of these complex ions in order to indicate their structure. Consider again the ferrocyanide ion, $Fe(CN)_6^{----}$. The six cyanide groups are here identical in their relationship to the iron atom, for they may be replaced by other groups, and no matter which one is replaced, the same compound results. They must be either linked to the central iron atom, giving the latter an apparent valency of six,



or they must be linked to each other in some such way as that illustrated below :—,



Of these, the first assumption is preferable, since the second is incompatible with the statement made above that all six (CN) groups are equivalent as regards replacement.

The consideration of a greater number of compounds of this type reveals the fact that the central atom of the complex ion frequently shows a maximum valency of six, though for some elements it may be four. The maximum valency appears to vary with the position of the element in the Periodic Table, as shown in the following Table.

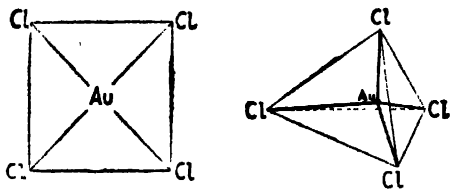
TABLE XXV

	Maximum Valency.
Hydrogen . . .	2
Lithium—Fluorine . .	4
Sodium—Bromine .	6
Rubidium—Uranium .	(rarely 8)

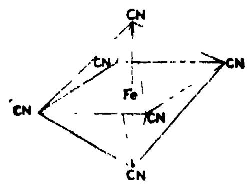
Alfred Werner, in 1891 and the following years, propounded a theory which was capable of explaining the behaviour of these molecular compounds. According to this theory, there was a tendency amongst certain atoms to attach to themselves a definite number of other atoms or groups, irrespective of their valency. The maximum number of groups that could be added was called the *co-ordination number*. It is usually four, or six. The atoms or groups thus attached were supposed to be in the first zone. Besides these, the molecule could contain other atoms or groups which were in a second or outer zone. These were not so firmly held, and could be ionised in water, whereas those in the first or inner zone could not. To return to the example of potassium ferrocyanide ; according to Werner, the substance could be written $K_4[Fe(CN)_6]$. The co-ordination number of the iron is 6, because the iron atom is surrounded by six cyanogen groups. These are in the first zone, and not dissociable. The whole group, $[Fe(CN)_6]$, or co-ordination complex (as it is called), can take up four potassium atoms, and these are in the second zone, and can be ionised in aqueous solution.

The spatial arrangement of these atoms and groups in the co-ordination compounds was also elucidated by Werner. The 4-co-ordinated compounds could have a planar or a tetrahedral structure.

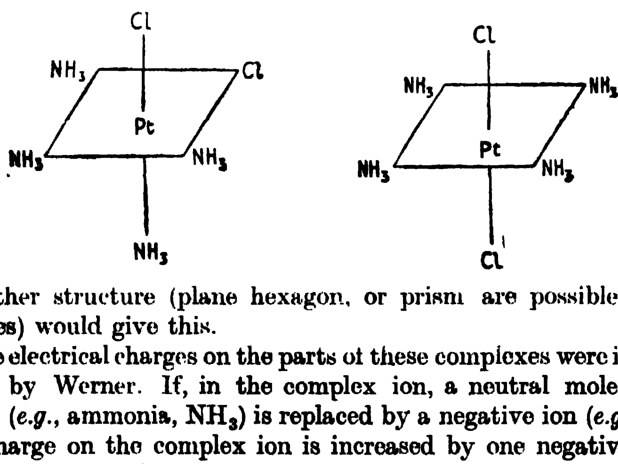
Here give also Fink's theory.



The 6-co-ordinated compounds must be octahedral.



This was verified by the fact that there are two isomers of compounds of the type [A_2MB_4], such as [$Pt(NH_3)_4Cl_2$], which differ considerably in colour, crystalline form, etc. On the octahedral theory they may be represented as



No other structure (plane hexagon, or prism are possible alternatives) would give this.

The electrical charges on the parts of these complexes were investigated by Werner. If, in the complex ion, a neutral molecule or group (*e.g.*, ammonia, NH_3) is replaced by a negative ion (*e.g.*, Cl^-), the charge on the complex ion is increased by one negative unit. Thus, if the complex is already positively charged to the extent of four units, it will be positively charged to the extent of three after the replacement. The following series of compounds may be prepared :—

$$[Pt(NH_3)_6]^{++++}Cl_4^{----}$$
$$[Pt(NH_3)_5Cl]^{+++}Cl_3^{---}$$
$$[Pt(NH_3)_4Cl_2]^{++}Cl_2^{--}$$
$$[Pt(NH_3)_3Cl_3]^{+}Cl^{-}$$
$$[Pt(NH_3)_2Cl_4]$$
$$[Pt(NH_3)Cl_5]^{-}K^{+}$$
$$[PtCl_6]^{--}K_2^{++}$$

The successive replacement of the neutral ammonia molecule by the electro-negative Cl^- decreases the charge on the complex ion, until the neutral compound $[Pt(NH_3)_2Cl_4]$ is reached, which does not ionise at all. Further introduction of Cl^-, and removal of NH_3, makes the whole complex ion electro-negative, and it is possible for it now to combine with an electro-positive metal like potassium.

The view that the central atom can take up a *number* of groups irrespective of their valency was quite foreign to the conception of valency held at the time (1890–1900), and the theory met with a poor reception. More recently, however, it has been shown to be essentially accurate, and the co-ordination compounds have received satisfactory explanation on the electronic theory of valency (§ 61).[1]

An important piece of work was that of Abegg in 1904, who returned to the idea that different valencies could be exhibited by an element, depending upon the element with which it was combined. He found that many elements had two kinds of valency which he called normal and contra-valency, and the sum of these was always eight. He called the maximum normal valencies positive for metals, and negative for non-metals. The contra-valency is of opposite polarity, and is much less frequently in evidence than the normal valency. The variation of these valencies with the group in the Periodic Table is shown in the Table below :—

TABLE XXVI

	Group in the Periodic Table. 1	2	3	4	5	6	7	8
Maximum Normal .	+1	+2	+3	±4	−3	−2	−1	0
Maximum Contra .	(−7)	(−6)	(−5)	±4	+5	+6	+7	+8

All these valencies are not always exerted. Thus chlorine is usually univalent, for example, in hydrogen chloride, but in chlorine heptoxide, Cl_2O_7, it is heptavalent, and is here exerting its maximum contra-valency.

59. The Electronic Theory of Valency.—With the advent of a more complete knowledge of the structure of the atom, the development of which has been outlined in Chapter II., came a much fuller idea of the meaning of valency. The old conception of valency as a number was gradually dropped, and attempts were made to find, in the modern theory of the structure of the atom, the reason for chemical combination. Valency is now regarded predominantly as a force, and not as a number.

[1] For an account of the preparation and properties of co-ordination compounds, see Ephraim, "Inorganic Chemistry" (Gurney & Jackson); a short account is given in "Inorganic and Theoretical Chemistry," Sherwood Taylor (Heinemann).

The electronic theory of valency owes its rise to the recognition of the existence of electrons in the atom. It was very soon suggested that electrons themselves were in some way responsible for chemical combination, and J. J. Thomson (1904) stated, as a pure speculation, that chemical combination was the result of a transfer of an electron from one atom to another.

In 1904, Drude, as a result of studying Abegg's "rule of eight," already mentioned, actually stated that "Abegg's positive valency number, v, whether it is a normal or contra-valency, signifies the number of loosely attached negative electrons in the atom: his negative valency number v' means that the atom has the power of removing v' negative electrons from other atoms, or at least of attaching them more firmly to itself."

In spite of the fact that the views then held on the structure of the atom differed considerably from those held at the present time, Drude came very near to our modern ideas.

It was necessary to wait for the full development of the idea of the nuclear atom before any advance could be made in the electronic theory of valency. In particular was it necessary to arrive at the concept of the atomic number (§ 34), which was done in 1913. This gave the number of electrons in each atom, and provided something to work upon in connection with valency.

Further developments came from two independent sources. Both Kossel and G. N. Lewis noted that the element which immediately precedes an inert gas in the Periodic Table is always strongly electro-negative and univalent. Thus chlorine immediately precedes argon, fluorine precedes neon, bromine precedes krypton, and iodine xenon. All these halogens are univalent and strongly electro-negative. Immediately following the inert gases, on the other hand, are always strongly electro-positive elements, and again they are univalent. They are, in fact, the alkali metals. These elements and the corresponding atomic numbers are shown in the Table below.

The fact that the inert gases are extraordinarily stable suggests that they contain a stable configuration of electrons. It is clear from the atomic numbers (Table XXVII.) that the halogens could all gain this stable configuration if they could take up one electron, and the alkali metals could attain the same objective by giving up one electron. When the atoms reach the stable configuration in this way they become the corresponding ions. Thus, potassium, when it loses one electron, will have a resultant unit positive charge, and will, in fact, be the potassium ion, K^+ (Chapter II., § 18). Fluorine, by gaining one electron, attains one negative charge, and becomes the fluorine ion, F^-. Extending this to the adjacent groups of the Periodic Table, calcium could give up two electrons

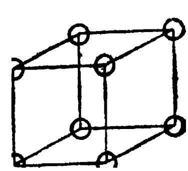
and attain the stable argon configuration; sulphur in Group VI. could take up two electrons and also attain the stable argon configuration. The ions Ca^{++} and S^{--} would thus be produced. The valency of the element is obviously the number of electrons which the atom must give up, or take up, in order to become possess d of a stable configuration. The electrons thus transferred are usually those in the outermost orbit, and are called *valency electrons*.

TABLE XXVII.—TABLE SHOWING ELEMENTS IN THE NEIGHBOURHOOD OF THE INERT GASES

Group VII.	Group 0.	Group I.
F (19·0)	Ne (20·2)	Na (22·997)
9	10	11
Cl (35·457)	A (39·91)	K (39·096)
17	18	19
Br (79·916)	Kr (82·92)	Rb (85·44)
35	36	37
I (126·932)	Xe (130·2)	Cs (132·81)
53	54	55

No atomic model whatever is involved in these statements. The only assumptions are that there are electrons in the atom; that each atom differs from the one preceding or following it in the Periodic Table by one electron, and that some of these are held more firmly than others.

When Lewis and Kossel put forward their theories, they assumed a static model for the atom. They looked upon the electrons as at rest, and stated that the stable configuration of eight was produced when the electrons occupied the corners of a cube. It is now known, however, that the electrons are in motion in certain orbits (Chapter III., § 53), and that the inert gases, which have stable configurations,



Ne

have eight electrons in their outermost energy level. Thus, the atomic constitutions of the inert gases are :—

Helium	2
Neon	2, 8
Argon	2, 8, 8
Krypton . . .	2, 8, 18, 8.
Xenon	2, 8, 18, 18, 8
Radon	2, 8, 18, 32, 18, 8

In every instance (except helium) the outermost level contains eight electrons (an octet), and this must be the number necessary to confer complete stability upon the atom. The other elements seek to attain these configurations by taking up electrons from other atoms that will part with them. Thus, in the formation of sodium chloride, the sodium atom, which has one electron above the number required for the stable neon configuration (its structure being 2, 8, 1), gives up this extra electron to chlorine, which has the structure 2, 8, 7, and could take it up to make the stable argon configuration. The electron is thus transferred from one atom to the other. This is represented as follows :—

$$[\mathrm{Na}]^{+}\left[\times\ddot{\underset{..}{\mathrm{Cl}}}:\right]^{-}$$

The dots represent the electrons of the outermost level, these being (as a rule) the only ones which play any part in deciding chemical combination. The cross represents the electron transferred from the sodium atom.

In the formation of a salt, such as sodium sulphide, which contains a divalent radical, the sulphur requires two electrons to reach the stable configuration. It can get these by combining with two sodium atoms, which will each supply one, or by combining with one calcium atom, which has two available electrons in the outermost level.

$$[\mathrm{Na}]^{+}\left[\times\ddot{\underset{..}{\mathrm{S}}}\times\right]^{--}[\mathrm{Na}]^{+} \qquad [\mathrm{Ca}]^{++}\left[:\ddot{\underset{..}{\mathrm{S}}}:\right]^{--}$$

When such a salt is dissolved in water, the very weak attraction between the constituent parts is destroyed, and two ions are produced. Thus, sodium chloride gives sodium and chlorine ions. These ions are merely the original atoms which have reached the state of stability by gaining or losing electrons. The electrons lost or gained give them their charge. Thus

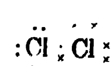
$$[\mathrm{Na}]^{+}\left[\times\ddot{\underset{..}{\mathrm{Cl}}}:\right]^{-} \qquad \mathrm{Na}^{+} + :\ddot{\underset{..}{\mathrm{Cl}}}:$$

The bond between the component ions of a metallic salt in which electrons have been *transferred* from one atom to another is called the *electrovalent* bond. Sometimes it is called a *polar* bond, but it is preferable not to use this term. The compounds are called electrovalent compounds.

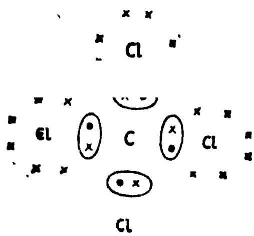
The electrovalent bond is very weak, even if it may be called a bond at all, for most crystalline salts are ionised even in the solid state. Two types of crystal structure are indicated by *X*-ray analysis (see p. 293) : one is typical of ionised compounds, in which the ions are closely packed in the crystal lattice, and the other is a neutral structure, much more open, found in substances like benzene, and ice. The *X*-ray examination of a substance like potassium chloride indicates that whilst the units in the space lattice are ions, the electrons are displaced from their orbits. In a certain measure a return to the dualism of Berzelius has been made in the conception of the electrovalent bond. More will be said about it later.

60. Covalent Linkages.—In organic, and in some inorganic substances, the linkage cannot be brought about in this way, for there will not be enough electrons to enable transference to be made. Thus, it is clear that in some compounds, such as the chlorine molecule, transference of electrons cannot have taken place. The transference of an electron from one of the chlorine atoms to the other (each having seven to start with) would allow one to attain the stable configuration, but would leave the other with six only.

Compounds of this type, too, are quite different from those that we have previously considered. They do not ionise, and as a rule they are much more volatile. To overcome the difficulty, it was supposed by Lewis that there was *sharing* of two electrons between the two atoms. In this way both could attain the stable structure.



Let us take another example. Carbon tetrachloride is obviously not at all similar to a metallic halide. It does not ionise, it does not dissolve in water, it is easily volatile. This is due to the fact that in this compound there are no unshared electrons, and only a small residual electric field. The electronic structure of this compound is given below. The electrons belonging to the chlorine are represented by crosses, and those to the carbon by dots, and the shared electrons are enclosed in rings.

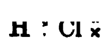


It will be seen that all the atoms have their full number of eight electrons, but they have only attained them by sharing electrons with other atoms.

A bond of this type, where one atom contributes one and the other also contributes one electron, is called a *covalent linkage*, or sometimes a *non-polar* linkage. The latter term is one to be avoided.

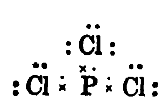
Covalent bonds are much stronger than electrovalent bonds, because the atoms are held together in some way by the shared electrons. In the case of the electrovalent bond, the ions are held together only by electrostatic forces. The electron has been given up, and except for some interaction of electric fields, the two atoms are free. According to Heitler and London, the formation of a covalent bond depends upon the resultant spin quantum numbers of the atoms (Chapter III., § 55). The sharing of electrons is, in effect, a neutralisation or coupling of the electron spins in the two atoms.

A few examples of substances formed by sharing electrons are given below :—

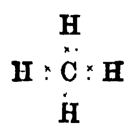


Hydrogen chloride
(in the gaseous state).

Water.

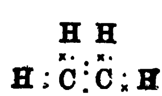


Phosphorus trichloride.



Methane.

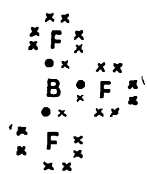
The double bond may be represented as the sharing of four electrons, as in ethylene



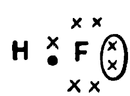
and the triple bond by the sharing of six, as in acetylene:—

H . C C : H

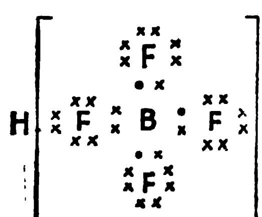
61. Co-ordinate Valency or the Semi-polar Bond.—Let us now consider what happens in the formation of such a compound as hydrofluoboric acid, HBF_4. This is made as a result of the combination of hydrogen fluoride, HF, with boron trifluoride, BF_3. On the electronic theory, boron trifluoride would be



It is seen that the boron can still take up two electrons to make its stable ring of eight. The fluorine atoms are satisfied, but the boron is still unsatisfied. Now, hydrogen fluoride is



and if it were permitted to share with the boron atom the two electrons enclosed in a ring, the latter would complete its octet. This is what is supposed to happen. The molecule

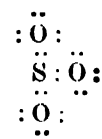


is thus formed; the hydrogen ionises off, and the radical BF_4 may be enclosed in brackets. The hydrogen has lost its original electron, and so is charged positively, whilst the BF_4 ion, as a whole, has gained it, and therefore becomes charged negatively.

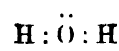
This type of bond is different from any so far considered, for it involves the sharing of two electrons which have both been supplied by the same atom. Since this process gives a satisfactory explanation of the co-ordination compounds of Werner, the bond has been called the co-ordinate bond, or the semi-polar bond, the latter being

a term proposed by Lowry, since there is transference, and at the same time sharing. To save time in writing, the co-ordinate bond is frequently written $A \rightleftarrows B$, or $A \longrightarrow B$. Hydrofluoboric acid is $HF \longrightarrow BF_3$.

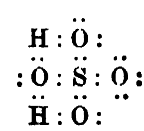
This may now be applied to other examples. It is interesting to see how it is that the radical XO_4 occurs so frequently in inorganic compounds, X being Cl, Mn, Cr, S, Se, Te, P, Si, etc. Let us take the formation of sulphuric acid from sulphur trioxide and water :—
Sulphur trioxide is



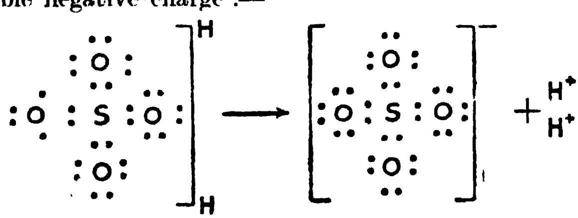
Water is



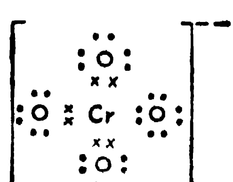
When the two come together we have



The hydrogen ionises off, and so we may write the[1] [SO_4] radical in square brackets, and the hydrogens outside. When the hydrogens are split off on dissolving the acid in water, they leave the radical with a double negative charge :—

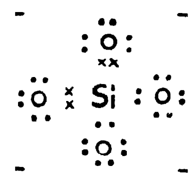


The $(CrO_4)^{--}$ ion is, similarly,



[1] The structure of H_2SO_4 is not necessarily as shown. It is written in this way for convenience in showing the SO_4 group.

The $(SiO_4)^{----}$ ion is



In every case, the octet of the central atom, X, of the ion (XO_4) is complete and fully shared. This is the reason for the stability of these ions. It also explains the comparative rarity of ions of the type (XO_5) and (XO_6). Periodic acid, H_5IO_6, is one of the few instances of a compound containing the (XO_6) ion.

The formation of salt hydrates, or the hydration of ions, is another example of co-ordination.

Lewis gave the name "acceptor" to any substance that could take up electrons to make its ring complete. Atoms which could supply them were called "donors."

62. The Electrovalent Bond and Ionisation.—The distinction between a metal and a non-metal is now shown more clearly. A substance is a metal, or shows metallic properties, when it can form positive ions, and hence when it can lose its valency electrons. A substance is a non-metal when it tends to take up electrons. It is for this reason that hydrogen shows both metallic and non-metallic properties. It travels to the cathode in electrolysis of acids, and takes the place of a metal in them, because it has given up its one electron. On the other hand, it can form hydrides, such as lithium hydride, LiH, which on electrolysis gives hydrogen at the anode. In LiH the hydrogen has taken up an electron to form the stable helium configuration, and is therefore acting as a non-metal. The fact that elements on the right-hand side of the Periodic Table are predominantly non-metallic (*e.g.*, oxygen, chlorine, sulphur, nitrogen, phosphorus, etc.), is explained because here the elements tend to take up electrons to attain the stable configuration of the next inert gas. The atoms of elements towards the left of the Table tend to give up electrons and attain the stable arrangement of the inert gas next before, and are therefore metallic in character (*e.g.*, sodium, aluminium, magnesium, calcium, etc.). A certain number of elements do not form ionisable compounds, or only do so with difficulty. These elements are in the middle of the Table. The best example is carbon. We may analyse into two factors the ease with which metals form ions. The first is the number of valency electrons. The higher the valency, the more difficult it will be to remove further electrons, after the first electron has been removed. In an

ion, there is the same nucleus as in the neutral atom, but fewer planetary electrons. Thus, as an electron is removed, the positive charge on the nucleus, which is unaltered by this process, has now a greater attractive effect on the remaining electrons. The more electrons are removed, the more firmly are the remainder held. Thus it becomes increasingly difficult to remove the electrons in polyvalent atoms.

The second factor is the atomic volume, which is governed by the size of the orbit of the valency electron. This will be further discussed in § 64.

62a. Transition Elements.—The question of the valency of the transition elements is interesting. Table XXVIII is taken from the atomic structure table on p. 136.

Starting with argon, which has a stable arrangement, the next element is potassium, in which the fourth quantum group begins to fill up. The third quantum group, however, is capable of holding eighteen electrons. After calcium, it begins to fill up, and instead of the additional electron being added to the fourth group, as might be expected, it is taken into the third. This is because the nuclear

TABLE XXVIII

At. No.	Element.	Structure.			
		Quantum-groups			
		1	*2*	*3*	*4*
18	A	2	8	8	
19	K	2	8	8	1
20	Ca	2	8	8	2
21	Sc	2	8	8, 1	2
22	Ti	2	8	8, 2	2
23	V	2	8	8, 3	2
24	Cr	2	8	8, 5	1
25	Mn	2	8	8, 5	2
26	Fe	2	8	8, 6	2
27	Co	2	8	8, 7	2
28	Ni	2	8	8, 8	2
29	Cu	2	8	18	1
30	Zn	2	8	18	2

charge, which also increases by one each time an electron is added, has become great enough to cause the electron to come into the stable 3_3 orbit. The additional electrons now continue to enter the

third group up to nickel (with the exception of manganese), and here the nuclear charge, 28, is still insufficient to keep the last two electrons in the third level, and they are to be found in the fourth group. Hence nickel is divalent in its ionisable compounds. With copper, the nuclear charge of 29 is capable of attracting these two electrons into the third group, and the 18 group is filled, leaving 1 outside. The true valency of copper is therefore 1, but the nuclear charge only retains the 18 group with difficulty, and chemical forces are able to extract another electron from the third group out into the fourth, thus making copper divalent in some of its compounds. In zinc and the higher elements in this series, up to krypton, the nuclear charge is capable of holding the 18 group against chemical forces, but similar behaviour is found later on in the Table in the next transition group. In this way we have an explanation of variable valency of the metals. Thus iron can have a valency of two or three, because chemical forces are capable of removing one of the electrons from the 18 group into the valency shell against the attraction of the nucleus. It is found to be more difficult to do this with cobalt, as the nuclear charge is greater, and so cobaltic salts are rare; and with nickel it cannot be done at all, and no nickelic salts exist. Summing up, we may say that variable valency depends on the fact that the attraction of the nucleus for the 3_3 electrons is not greatly different from that for the 4 electrons, so that chemical forces are able to move electrons from the 3_3 orbit to the 4_1 orbit, thus increasing the valency.

Another interesting point connected with this variable valency is the colour of the ions. All the elements from titanium to copper in the above series have coloured ions. If an ion is coloured it means that it absorbs light in the visible spectrum. If this is the case, transitions must take place in the atom which correspond to the absorption of quanta of visible light, of which the energy is between about 40,000 and 70,000 gram-calories per gram atom. In the case of an ion with a completed ring, such as Ca^{++} (of which the structure is 2, 8, 8) or K^+ (of which the structure is again 2, 8, 8), the only transitions that can take place are those to a higher orbit. The amount of energy required for this would be considerably greater than 70,000 gram-calories per gram atom. Consequently these ions absorb in the ultra-violet (corresponding to a large quantum), and appear to be colourless. In the case of an ion, or atom, with an incomplete ring, *e.g.*, sodium in the molecular form (of which the structure is 2, 8, 1, wanting 7 to complete the 8 of the third orbit), it is possible for the odd electrons in the incomplete outer ring to undergo transitions in the same energy level, *e.g.*, from 3_1 to 3_2, and the atom can thus absorb in the visible region. The vapour of

sodium actually absorbs in the yellow. The sodium ion would have a completed outer ring (2, 8), and consequently transitions would have to occur from 2 to 3, involving a good deal of energy, and therefore absorption in the ultra-violet. In general, then, those atoms and ions will be coloured which have incomplete outer rings. We have this in the group of transition elements we have been considering. When ionised, the atoms still possess an incomplete third ring. Thus, the cupric ion is blue. Here the structure is 2, 8, 17. Transitions, involving small amounts of energy, can therefore take place in the third orbit itself. The cuprous ion, however, is colourless. Its structure is 2, 8, 18. The third group is complete, and transitions can only take place to higher quantum-groups involving the absorption of large amounts of energy.

The magnetism of the ions of this group is also bound up with the existence of the incomplete rings. The ions of the elements from scandium to copper are all paramagnetic (*i.e.*, bodies containing these ions tend to set themselves parallel to the lines of force of the magnetic field ; ferromagnetism is a special case of paramagnetism. Diamagnetic bodies tend to set themselves perpendicular to the field). It is known that ions with completed groups are diamagnetic ; this may be due to a balancing of the magnetic moments of the orbits. Ions with incomplete groups are paramagnetic, as the magnetic moments are unbalanced.

The valencies of certain non-transition elements, particularly the B elements of Groups III., IV., V., VI. and VII., are abnormal. As examples, the elements thallium, lead, and bismuth, may be taken ; whilst mercury, although not falling in the above groups, may be added, since it shows similar abnormalities. If the electronic structures of these elements are written down (Table XXIX.), it is seen

TABLE XXIX.—STRUCTURES OF Hg, Tl, Pb, Bi

Orbits.	1–5.		6_{11}	6_2
80 Mercury .	60,	18,	2	
81 Thallium .	60,	18,	2	1
82 Lead. .	60,	18,	2	2
83 Bismuth .	60,	18,	2	3

that the valency of mercury should be two ; of thallium, three ; of lead, four ; and of bismuth, five, or three if it makes up its octet. The valencies actually exerted are : mercury, two ; thallium, one

and three ; lead, two and four ; bismuth, three, four and five and, possibly, two. Why is this ?

It is now known that the first two electrons in any group, having the quantum numbers N_{11}, behave differently from the rest, as they correspond to the 1_{11} electrons in helium. They form a subsidiary stable arrangement, and may be difficult to ionise, or even to share. They are called an "inert pair."

In the instance of mercury, the mercurious ion has been shown by Ogg, and others, to be $[Hg_2]^{++}$ and not $[Hg]^{+}$. In the mercury atom, the structure ends with two 6_{11} electrons, and if the theory of the "inert pair" is correct, mercury should be a comparatively inert element. The structure of the mercurous ion is evidence for this. In this, there are two mercury atoms sharing two electrons, thus giving the "ion" two positive charges. Since the 6_{11} electrons can link together the two mercury atoms, they form covalent rather than electrovalent linkages. This is shown again in the unusual fact that mercuric salts are, on the whole, little ionised. They are predominantly covalent compounds. The conductivity of a solution of mercuric chloride is much smaller than that of an equivalent solution of, say, cadmium chloride.

With thallium, the two 6_{11} electrons and the one 6_2 electron can be used for covalencies, but only the 6_2 electron can be used for electrovalencies. Thus, the thallous salts are ionised, but the thallic salts are all covalent, and do not ionise. With lead, the bivalent compounds, such as lead nitrate, $Pb(NO_3)_2$, are electrovalent and ionised in solution, whilst the quadrivalent compounds, such as lead tetrachloride, $PbCl_4$, are definitely covalent. ?

In bismuth the two 6_{11} electrons are similarly inert as regards valency, for bismuth never forms electrovalent compounds with a valency greater than three. Tin shows similar behaviour to lead. Its structure is 2, 8, 18, 18, 2, 2 ; the two 5_{11} electrons are an inert pair. The quadrivalent salts of tin, such as stannic chloride, are covalent, whilst the bivalent salts, such as stannous chloride, are electrovalent.

63. Distinction between Electrovalent and Covalent Compounds. It has already been noted that the electrovalent bond is much weaker than the covalent bond (§ 60). Ionisation occurs in compounds containing the former, not only in solution, but also in the solid state.

In an electrovalent compound there will be no definite structural bond, but a strong residual electric field, and so the work done in separating molecules will be greater than the work required to separate molecules in covalent compounds. This means that the boiling point of an ionised compound will be much higher than that of a covalent compound, and this is found to be so in the vast majority

of cases. Thus carbon tetrachloride may be compared with common salt. The boiling point of the former is 78° C., whilst that of the latter is over 1,000° C. Or, compare stannic chloride, which is a liquid, and potassium chloride. The first is a typically covalent compound, the latter a typically electrovalent compound.

It is found, too, that covalent compounds are soluble in normal solvents (see p. 274), such as benzene and ether, whereas electrovalent compounds are soluble in abnormal liquids like water, which cause ionisation.

Lewis pointed out that linkages always appeared to involve two electrons—electron pairs, he called them. It is possible, however, that single electron linkages can exist. One instance where the existence of singlet linkages has been postulated is in the hydrides of boron. A series of these has been investigated by Stock, and the hydrides are found to have the formulæ corresponding to the hydrocarbons. The most common boron hydride has the formula B_2H_6, which, by analogy with ethane, would be expected to be derived from a tetravalent atom. Boron, however, is trivalent. One way of explaining the existence of these compounds is to assume that some of the hydrogen atoms are linked to the boron by singlet linkages, as the following formula shows :—

$$\begin{array}{ccccccc} & & H & & H & & \\ & & \overset{\cdot\times}{} & & \overset{\cdot\times}{} & & \\ H & \overset{\times}{\cdot} & B & : & B & \underset{\times}{\cdot} & H \\ & & \times & & \times & & \\ & & H & & H & & \end{array}$$

The structure of the boron hydrides is still, however, an open question.

64. Fajans' Rule.—When the electrical conductivities of the chlorides of the elements are determined in the fused or liquid state it is possible to classify them into two distinct classes—those which conduct well, and those which conduct badly. If these are put down with the positions of the elements in the Periodic Table, as in the following table, it is seen that the ionised chlorides are sharply distinguished from the non-ionised chlorides and separated from them by a line which goes step-like across the table from left to right. Those elements above the line obviously form covalent chlorides, those below it electrovalent chlorides. Anomalies are enclosed in dotted lines.

Fajans' rule concerns the occurrence of electro- and co-valencies, and its connection with the position of the element in the Table. It states that the formation of electrovalent linkages is promoted by a high atomic volume (atomic weight divided by specific gravity) for the cation as compared with the anion, and by small ionic charges.

There is considerable theoretical basis for this. It is clear that the larger a metallic atom the less will be the attractive force for the outer electrons. They will not be held so strongly by the nuclear charge. The formation of a cation is thus helped by a large atomic volume, and of an anion by small atomic volume. The formation of multivalent anions (with the exception of complex ions, such as $[Fe(CN)_6]^{----}$) is an extremely difficult matter, since every addition of electrons makes the nuclear attraction smaller. A simple analogy is that of a magnet picking up nails successively. As each one is added the attraction for more gets less. It is for this reason that the maximum valency for a simple anion is two, whilst the valency of a cation can go up to four. Summing up, the conditions tending to produce electrovalent and covalent compounds are as follows :—

TABLE XXX.—EQUIVALENT CONDUCTIVITIES OF CHLORIDES AT THE MELTING POINT

Group I.	II.	III.	IV.	V.	VI.
HCl $<10^{-6}$					
$LiCl$ 166	$BeCl_2$ 0·086	BCl_3 0	CCl_4 0		
$NaCl$ 133	$MgCl_2$ 28·8	$AlCl_3$ $1·5 \times 10^{-5}$	$SiCl_4$ 0	PCl_5 0	
KCl 103	$CaCl_2$ 51·9	$ScCl_3$ 15	$TiCl_4$ 0 $SnCl_4$ 0	VCl_4 0	
$RbCl$ 78·2	$SrCl_2$ 55·7	YCl_3 9·5	$ZrCl_4$?	$NbCl_5$ 2×10^{-7}*	$MoCl_5$ $1·8 \times 10^{-6}$*
$CsCl$ 66·7	$BaCl_2$ 64·6	$LaCl_3$ 29·0	$HfCl_4$?	$TaCl_5$ 3×10^{-7}*	WCl_6 2×10^{-6}*
	$HgCl_2$ $2·5 \times 10^{-3}$	$TlCl_3$ $<2·5 \times 10^{-4}$	$ThCl_4$ 16		UCl_4 0·34*
	Hg_2Cl_2 40 (approx.)	$TlCl$ 46·5			

* Specific conductivity.

Electrovalent.	Covalent.
Low charge.	High charge.
Large positive ion.	Small positive "ion."
Small negative ion.	Large negative "ion."

It must be mentioned that whilst Fajans' rule is very helpful, it is not without exceptions.

The alkali metals (lithium, sodium, potassium, rubidium, and cæsium) form good examples of the application of Fajans' rule. The atomic volumes of these elements are shown in the Table.

TABLE XXXI.—ATOMIC VOLUMES OF THE ALKALI METALS

Metal	Li	Na	K	Rb	Cs
Atomic Volume	11·8	23·7	45·3	56·0	70·7

The atomic volumes of the last three elements are very large. This means that the valency electrons have large orbits, and will be comparatively easily detached. The charge, of only one unit, on the ion, also adds to the ease of ionisation, according to Fajans' rule. Thus, it is very difficult for these elements to form covalent links, except for lithium and sodium. Hydration of salts is an indication of formation of a co-ordinate link, as in solvation of ions (§ 61). Accordingly, it is found that the salts of lithium are nearly all hydrated, and so are many of those of sodium, thus showing the capacity of these elements to form covalent linkages (for a co-ordinate linkage is merely a form of covalent linkage). The salts of potassium, however, are seldom hydrated, whilst it is rare to find hydrated salts of rubidium or cæsium.

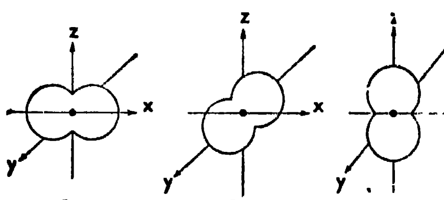
Beryllium, in Group II., has an atomic volume of only 4·92, and a charge of 2 units. It is on the limit of ionisation, as would be expected from Fajans' rule. Beryllium chloride is a very poor conductor in the fused state, though it is ionised in water. It is therefore covalent in the solid state, but electrovalent in solution. Magnesium has a higher atomic volume (14·0), and though still capable of forming complexes, its compounds are predominantly electrovalent, and it resembles the alkaline earth metals much more than beryllium does.

In Group III., boron is unable to form a simple cation, owing to its small size (atomic volume, 4·11). Aluminium, having a larger atomic volume than beryllium (10·2), can form a tervalent cation, though the high charge (3) makes it form covalent compounds readily. Thus, aluminium chloride is a covalent compound in the solid state. It will readily dissolve in normal liquids, such as benzene.

An ion with a charge of 4 units could only exist if it were unusually large, and so none of the early elements in Group IV. are found to give electrovalent compounds. The first quadrivalent ion is found with tin (atomic volume 16·5).

65. The Nature of the Covalent Bond.—As stated in Chapter III., there are two fundamental features about an electron in the atom.

They are the energy level in which the electron is to be found, given by the quantum number n, and the type of orbit in which it is moving, given by the quantum numbers k and j. The energy shells or levels are denoted either by a number or a letter. Thus, the K level has quantum number $n = 1$, the L level has $n = 2$, the M level has $n = 3$, and so on. The type of orbit, or orbital as it is sometimes called, is often represented by the letters s, p, d, and f, from the nature of the spectrum emitted by the excited atom when electrons in these orbits are involved (§ 52). The s-orbits are spherically symmetrical, so that there is only one such orbit for any particular level. In the case of the p-orbits, it is possible to have three stable ones at any one level (except the first level, where, of course, the s-orbit is the only one). These three p-orbits have



$2p_x$ $2p_y$ $2p_z$

FIG 47a

their axes mutually at right angles, and are sometimes called the p_x, p_y, and p_z orbits. There are five possible d-orbits, and seven f-orbits. The distribution of the electrons in a normal atom may be written shortly by making use of these letters and numbers. Thus, the normal nitrogen atom has the configuration $1s^2 2s^2 2p^3$, meaning that there are two electrons in the s-orbit of the first level, two s-electrons in the second level, and 3 p-electrons in the second level. Actually the three p-electrons are arranged one in each of the three types of p-orbit, and to make this clear we could write the configuration $1s^2 2s^2 2p_x 2p_y 2p_z$. The total of the indices must be the number of electrons in the structure, *i.e.*, the atomic number of the atom. In the case of nitrogen this is 7. A few other examples are appended :

argon	$1s^2 2s^2 2p^6 3s^2 3p^6$	a total of 18 electrons.
potassium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$	a total of 19 electrons.
chlorine	$1s^2 2s^2 2p^6 3s^2 3p^5$	a total of 17 electrons.

These can be checked against the figures given in the table of atomic configurations on p. 136.

The number of electrons in any one orbit is limited by the *Pauli exclusion principle* (§ 55), which states that it is impossible for more than two electrons to exist in any one orbit. When an orbit

contains two electrons they must differ in some way, otherwise it would be impossible to distinguish between them and to prove that two were actually there. The difference between the electrons in an orbit lies in their spin. One has a clockwise spin, the other an anticlockwise spin. Electrons with opposite spins are said to have anti-parallel spins.

The phenomenon of magnetism is associated with electron spin. If an atom or molecule contains electrons with un-neutralised spins (*i.e.*, if the spins of the two electrons are parallel, or if there is an odd electron) it is paramagnetic. Thus, we find that the free hydrogen atom is paramagnetic; it contains only one *s*-electron. The hydrogen molecule, on the other hand, is diamagnetic. It is thus concluded that the formation of an electron-pair bond, or a covalent bond, takes place between electrons of opposite spin.

This appears to be the necessary condition for the formation of a stable covalent link. For combination to occur there must be at least one " free " electron (*i.e.*, an electron of which the spin is not neutralised). Those electrons which are paired in the atom (so-called " restricted " electrons) cannot enter into links with other atoms unless, as we shall see below, a process called hybridization takes place. In this connection, electrons in the three different *p*-orbitals, though they may have contrary spins, do not neutralise each other.

Hydrogen, with one stable orbital, can form only one covalent bond, contrary to earlier views. In helium we have two *s*-electrons, with necessarily anti-parallel spins because they are in the same orbital. This atom will therefore show no tendency to combine with other atoms in its normal state. If one of its electrons were raised to a higher level by excitation, we should have an entirely different state of affairs, and it might be possible to obtain compounds of helium under those conditions; some indeed have been reported, though they are naturally unstable. In lithium, we have the configuration $1s^22s$, with one unpaired electron in the 2-level. The valency of this atom will therefore be 1, since the 2*s* electrons in the first level have opposite spins and are not available for forming covalent links with other atoms. Difficulties are encountered, however, with this simple theory as it stands, when we come to the element beryllium, which has the configuration $1s^22s^2$. All its electrons are already paired and it should be inert like the inert gases. Similarly carbon, with the configuration $1s^22s^22p^2$ would only have a valency of two, as the only unpaired electrons are the 2 *p*-electrons, being in different *p*-orbits. This is contrary to all chemical experience. The valency of carbon is undoubtedly four. In order to achieve this result it is necessary to suppose that when combination occurs, one *s*-electron is pulled out to the *p*-orbit,

giving $2s2p^3$. Since three electrons can be accommodated in the p-orbits and none of the spins are neutralised, we now have four free electrons, sufficient to account for the quadrivalency of carbon. But this, in itself, is insufficient. A study of organic chemistry leads indubitably to the fact that the four carbon bonds are identical. They could not be if one involved an s-electron and the others three p-electrons. The four orbits must therefore be made equivalent. Consideration of the mathematics of the problem leads to the view that this is not impossible, and is a process called hybridization. It is now necessary to see whether this process gives the correct stereochemical relationships. The carbon atom has tetrahedral symmetry, and it can be shown that the spatial direction of the bonds arrived at by the process of hybridization agrees with this, although it must be admitted that an alternative configuration with three orbits directed towards the apices of an equilateral triangle, and a fourth, weaker in bonding strength, at right angles to the triangle, is also a possibility from the theory.

This hybridization process may be supposed to occur in beryllium, the $2s^2$ electrons becoming $2s2p$. These two electrons in the L-level may now have the same spins, and both will be available for the formation of covalent links, the beryllium atom being thus divalent. Similar treatment of other atoms, which in the free, normal state have electrons with paired spins, leads to results in agreement with the chemical and stereochemical facts.

It will be noted that in the quantum method of treatment, the idea of the stable octet of electrons loses its significance. The importance of this will be seen later (§ 67).

In the above we have referred to the term "orbit". It is necessary to remember, however, that in fact we cannot state just where an electron is, though we can say that it is very probable that it is to be found in a given element of volume. The "orbits" are therefore not lines which the electrons traverse, they are rather surfaces enclosing volumes in which the electron is very likely to be found. As stated above the s-orbit is a sphere, while the three p-orbits are dumb-bell shaped. When two atoms combine to form a molecule, the electrons forming the link now move round both nuclei. In the simplest case,

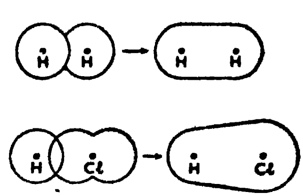


FIG. 47b.

that of the hydrogen molecule, the electrons in the single hydrogen atoms are in the s-orbit. In the formation of the molecule, these orbits overlap, and combine to form one which contains both nuclei, and is sausage-shaped. To take another simple case, that of hydrogen

chloride. The hydrogen atom has an electron in the *s*-orbit. The valency electrons of chlorine are in the *p*-orbit. There is overlapping of the orbits, and the resulting bicentric orbit is as shown in Fig. 47b.

It is impossible here to enter into a fuller account of the quantum theory of valency. Although much work has already been done on this method of attacking the problem, there are still many difficulties to be cleared away. This is largely due to the mathematical difficulties associated with the solution of the wave-equations for complicated atoms. At present a good deal of the work is in the qualitative stage.

66. Resonance.—It has been stated that the formation of a bond results from the overlapping of the valency orbits, the electrons taking part in the bond having opposing spins. It is usually easy to see which atoms will take part in this sharing and overlapping, but there are cases where there are possible alternatives. Consider the benzene molecule, C_6H_6. This is a plane, hexagonal molecule, and each carbon atom is linked to one hydrogen atom. When this has been done, each carbon atom still has one electron in a *p*-orbit,

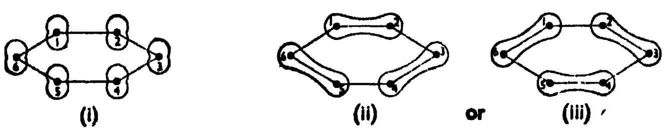


FIG. 47c.

as shown in Fig. 47c (i.). Now it is impossible to say whether the *p*-electron of carbon atom 1 will overlap with that of 2, or with that of 6, so there are two possible ways in which the overlapping could take place throughout the ring, these two ways being represented by (ii.) and (iii.) in Fig. 47c. This means that benzene should behave as if the double bonds were partly in one position and partly in the other.

The problem of what to do with the double bonds in the benzene molecule has always been a difficult one. Kekulé assumed that the bonds alternated, being first in one position and then in the other. The quantum-mechanical theory would say that the double bonds are actually in neither position, but that the substance acts as if they were partly in one and partly in the other.

Where this state of affairs occurs, the phenomenon is called quantum-mechanical resonance. This term "resonance" is used because the whole conception is the outcome of the wave-theory of the electron, and the equations are similar to those governing resonance in classical mechanics. There is actually a close analogy with the mechanical system comprising two pendulums vibrating in resonance, and in agreement with the principles of mechanics,

it has been shown that the resonating structure has a smaller inherent energy than any of the structures taking part in the resonance.

We may define quantum-mechanical resonance as follows : When the electrons in a molecule may be paired together in two or more different ways which differ only slightly in energy content, the actual molecule does not behave as if it possessed any one of the structures, but is a resonance hybrid of them all, showing simultaneously properties characteristic of each separate structure.

In the case of benzene, the theory of resonance has been confirmed by determining the distance between the carbon atoms. On the alternation theory of Kekulé, the bond should vary in length from 1.54 Å (the length of the single C—C link) to 1.34 Å (the length of the double bond C = C). According to the resonance theory the length should be intermediate between the two. X-Ray determinations actually give it as 1.39 Å.

As a further example we may take the nitrous oxide molecule. Experiment shows that this molecule is linear, with the oxygen atom at the end of the line. There are two likely structures which fulfil this condition, $\overset{-}{N} = \overset{+}{N} = O$ and $N \equiv \overset{+}{N} - \overset{-}{O}$, the + and − signs indicating the polarity of the molecule. These two structures can be shown to differ only a little in energy, and have the necessary conditions for resonance. It is believed then that nitrous oxide is not actually represented by either structure. That this is true is clear from experiment, which indicates that the molecule does not possess a large dipole moment, as it would have if it were markedly polar as required by either of the above structures.

It should be emphasised that nitrous oxide is not a tautomeric mixture of molecules with these two structures. Statistically, the real structure is something intermediate between the two, which cannot, in fact, be represented by the conventional diagrams. The stability of nitrous oxide is to be ascribed to the fact that the energy of the resonating system is less than that of either structure separately.

The structure of carbon dioxide is somewhat similar to that of nitrous oxide. Here the resonating structures are $O = C = O$, $O^{+} \equiv C - O^{-}$ $- C \equiv O^{+}$.

The theory of resonance applies equally well to polar and non-polar structures as to two polar structures. Thus, hydrogen chloride can be represented both as a covalent and an electrovalent compound :

$$H \overset{\times}{\cdot} \ddot{\underset{\cdot\cdot}{Cl}} : \qquad \text{and} \qquad H^{+} \; \overset{\cdot}{\times} \ddot{\underset{\cdot\cdot}{Cl}} :^{-}$$

It is supposed that there is resonance between the two structures, so that the molecule is neither completely polar nor completely ionic.

The theory has been applied to a large number of chemical problems with success.

66a. The Hydrogen Bond.—Hydrogen behaves in a peculiar way in a number of compounds, and was at one time thought to be capable of forming a stable ring of four electrons. This is now known to be impossible, but the theory of resonance has explained how hydrogen can be attracted towards certain other atoms fairly strongly, so that it may be supposed to act as a bond or bridge between them.

Experiment shows that water is associated. At ordinary temperatures the molecule consists of aggregates of three simple H_2O molecules. This simple molecule is represented on the electronic theory as

$$H \overset{\times}{\cdot} \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \overset{\times}{\cdot} H \quad \text{or} \quad H - O - H.$$

The hydrogen can form a " hydrogen bond " with the oxygen atom of another H_2O molecule, thus

$$\begin{array}{c} H \\ | \\ H - O - H \cdots\cdots O \\ | \\ H \end{array}$$

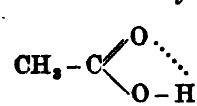
This may go on with the " addition " of another molecule of H_2O.

As far as theory is concerned, it is evident that this adding of H_2O molecules could go on indefinitely. It comes to a stop, however, when the thermal vibrations of the molecule become large enough to prevent it. At ordinary temperatures, then, the aggregate contains, as a rule, three simple molecules, and as the temperature is raised the proportion of dimeric molecules increases, and that of trimeric molecules decreases. The degree of association of water at different temperatures is given in the table in § 117.

Hydrogen fluoride is also associated for a similar reason.

$$H - F \cdots\cdots H - F \cdots\cdots H - F.$$

Hydrogen bonding occurs in the carboxylic acids,



and accounts for the fact that the carbonyl group, $C = O$, has different properties in these acids, from those which it possesses in the aldehydes and ketones.

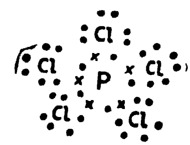
The hydrogen bond may be considered as a case of resonance, the hydrogen atom forming the bridge being first nearer the one

Read also "metallic bond

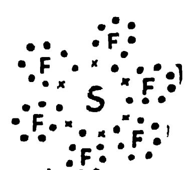
atom and then the other between which the bridge exists:

$$R:H\ \ :R^1 \rightleftharpoons R:\ \ H:R^1$$

67. The Validity of the Octet Rule.—The octet rule is found to hold for many elements at the commencement of the Periodic Table, *e.g.*, in the lighter elements, the number of electrons which can exist in the valency level is limited to eight. But proceeding down the series, it is found that if the idea that sharing always takes place with pairs of electrons is to be retained, it is necessary to expand the valency group. Thus, if phosphorus pentachloride is written as a covalent compound, as it really is, the structure



is obtained, in which the phosphorus is surrounded by ten electrons. In the case of sulphur hexafluoride, SF_6, it is necessary to have twelve electrons in the valency level, if sharing is to take place between pairs.



This increase in the number of electrons available for sharing is explained by the process of hybridization referred to above. The maximum number of these electrons will clearly depend on the number of stable orbitals present in the structure of the atom, and will increase as the periodic table is ascended.

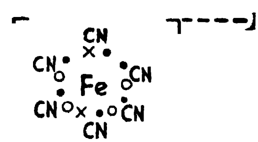
The number of covalencies that the elements can have as a maximum is given in the Table below:—

TABLE XXXII

	Max. Number of Covalencies.
Hydrogen . .	1
Lithium to fluorine	4
Sodium to yttrium .	6
Zirconium to uranium	8[1]

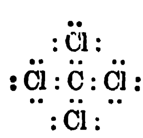
[1] With possibly 10 in the heavier elements.

The formation of many complex ions demands an increase in the number of electrons in the valency ring if electron sharing always takes place in pairs. Thus, consider the formation of the ferrocyanide ion $[Fe(CN)_6]^{----}$. The iron has two electrons of its own represented by crosses. The cyanide group has one valency electron represented by a dot. The first two cyanide groups to be taken up may be supposed to share their electrons with those of the iron. Four other cyanide groups are taken up, and in order to supply the other electrons to make pairs, four must be added from outside represented by circles), *e.g.*, from four alkali metal ions. These make the ion quadrivalent.



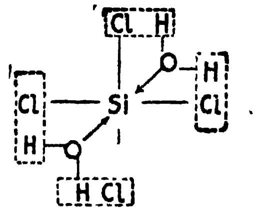
The iron atom is now surrounded by twelve electrons.

By means of the theory that covalency can be increased to a certain maximum for different elements it has been possible to explain numerous otherwise seemingly inexplicable reactions of inorganic chemistry. As an example, the action of water on the non-metallic halides may be taken. Carbon tetrachloride is not affected by water. This is because the maximum number of electrons that the carbon atom can provide in its valency group is 8, and this number has already been reached by the mere addition of the chlorine :—



The carbon therefore cannot act as an acceptor or donor, and water or alkali has no action upon the compound. Considering sulphur hexafluoride, SF_6, a similar behaviour is found (see formula above). The covalency maximum for sulphur is 6, and so it can have twelve electrons in its valency level. These are already present in sulphur hexafluoride, and so no reaction between this compound and water will be expected.

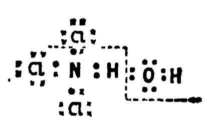
Silicon tetrachloride acts differently. When acted upon by water, hydrogen chloride is evolved, and silica is left. Silicon tetrachloride may be represented as



From this compound hydrogen chloride splits off, and silica, O=Si=O, is left.

The theory thus provides a good explanation of why carbon tetrachloride is unaffected by water, whilst its analogue, silicon tetrachloride, is decomposed by it.

Compounds like nitrogen trichloride, NCl_3, and chlorine monoxide Cl_2O, behave in a different way as regards hydrolysis. Instead of hydrogen chloride being split off, hypochlorous acid, HOCl, is removed. In nitrogen trichloride, the octet of the nitrogen cannot expand, but it has a pair of electrons available for sharing (called by Lewis a " lone pair "). It therefore co-ordinates as a donor with water, whereas silicon tetrachloride co-ordinated with it as an acceptor. The hydroxyl group now comes away with chlorine as hypochlorous acid.



There are many other points that can be well explained by the electronic theory. Thus, Lewis pointed out that many elements in the second short period of the table differ from those in the first, in providing compounds which tend strongly to polymerise. Thus, carbon in the first group forms carbon dioxide and carbonic acid. Compare these with silica and silicic acid. The former show no tendency to polymerisation, whereas silicic acid can easily be obtained as a gel of high molecular weight (Chapter XVII.). Then again the molecules of oxygen and of nitrogen are O_2 and N_2, whereas those of the members of the second short period are S_8 and P_4. These facts are readily explained on the theory of covalency maximum. The carbon in carbon dioxide is fully satisfied, and the ring cannot expand, but silicon can have a ring of twelve electrons, and this is not attained in silica. Hence co-ordination can occur, and associated molecules are formed (*cf.* the

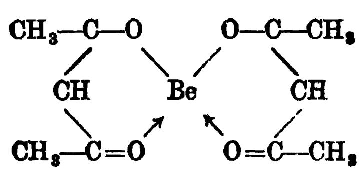
association of water). The large molecules of sulphur and phosphorus are similarly explained.

The stability of carbon chains compared with those of silicon receives an explanation if the covalency maximum theory is accepted. Saturated carbon chains, such as $-CH_2-CH_2-$ are not attacked by water, whereas the corresponding chains of silicon are, with the entrance of oxygen into the chain. Thus

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{|}{\underset{|}{\mathrm{Si}}}- + H_2O = -\overset{|}{\underset{|}{\mathrm{Si}}}-O-\overset{|}{\underset{|}{\mathrm{Si}}}- + H_2$$

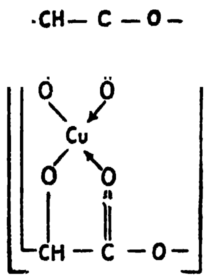
This is due to the fact that silicon, in view of the possible expansion of its valency group, can act as an acceptor.

68. Chelate Compounds.—There are some peculiar metallo-organic compounds, in which there is internal co-ordination, which receive satisfactory explanation in terms of the electronic theory of valency. These compounds are called chelate compounds. In them a metal atom which might be expected to form an ion does not do so, but co-ordinates with another atom, usually ogygen. The metallic derivatives of the diketones fall into this class. The beryllium compound of acetylacetone $CH_3.C(OH):CH.CO.CH_3$, may be represented as follows :—



The beryllium has its octet satisfied, and the compound is covalent.

A similar chelate group is probably present in Fehling's solution. This solution is prepared by adding a solution containing sodium hydroxide and sodium potassium tartrate to one of copper sulphate. In the absence of the tartrate the addition of the sodium hydroxide would precipitate copper hydroxide. With the tartrate, however, a deep blue solution is obtained, containing a complex copper ion which probably has the structure



SUMMARY

Development of the Theory of Valency.—The first theory of valency (the dualistic theory) was propounded by Berzelius, who supposed that the atom possessed an electrical charge, of which the sign varied with the nature of the element. Combination occurred when oppositely charged atoms came into contact, and resulted in the partial neutralisation of the charges. Oxygen and chlorine were negatively charged, whilst hydrogen and the metals were positively charged. Dumas showed that the substitution of chlorine for hydrogen in acetic acid, to produce chloracetic acid, did not greatly modify the properties of the acid. He therefore concluded that hydrogen and chlorine were not sufficiently dissimilar to warrant their possession of opposite electrical charges. Instead of the dualistic theory, he proposed a theory of types, which was later improved by Gerhardt. All compounds could be formulated by substituting elements or radicals for hydrogen in the four types.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H\\H\end{matrix}\right\} \qquad \left.\begin{matrix}H\\Cl\end{matrix}\right\}$$

to which Kekulé added a fifth.

$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C.$$

Williamson used the idea of mixed types.

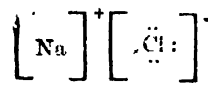
Frankland believed that elements could combine with others until "saturated." Every element had a saturation value, or valency, defined as the number of atoms of another element or radical which could combine with one atom of the original element.

From this developed the theory of valency which stated that the valency of an element was the number of atoms of hydrogen with which one atom of the element could combine. This is also equal to the atomic weight of the element divided by the equivalent.

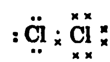
In order to explain molecular compounds, such as potassium ferrocyanide, $K_4[Fe(CN)_6]$, Werner assumed that elements could combine with a certain number of atoms or groups, irrespective of their valency.

This number was usually 6 or 4, and was called the co-ordination number. By his theory he was able to explain the isomerism of co-ordination compounds, and the electric charge on their constituent parts.

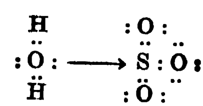
The electronic theory of valency arose from the application of the quantum theory of the structure of the atom to the problem of chemical combination. Combination takes place: (1) by the transfer of an electron from the orbit of one atom to that of another. This is called an electrovalent linkage, and the compound formed is ionised, *e.g.*, as in sodium chloride.



(2) By sharing of two electrons between two atoms, *e.g.*, as in the chlorine molecule.



This is called a covalent linkage, and is not ionisable. (3) By one atom supplying two electrons which are shared between the two atoms. This is called a co-ordinate linkage, or a semipolar bond, *e.g.*, as in sulphuric acid.



In the simplest case, each atom has a completed ring of eight electrons (an octet) after combination, but it has been found necessary to increase this ring for the heavier elements. The maximum number of electrons which can appear in the valency level of different elements is H, 4; Li – F, 8; Na – Y, 12; Zr – U, 16.

Fajan's rule states that the formation of electrovalent linkages is promoted by a high atomic volume for the cation as compared with the anion, and by small ionic charges. Electrovalent compounds may be distinguished from covalent compounds by (1) their ionisation, (2) their much smaller volatility, (3) their solubility in ionising solvents (*e.g.*, water) and insolubility in non-ionising solvents (*e.g.*, benzene).

SUGGESTIONS FOR FURTHER READING

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Palmer, W. G. "Valency." (*Cambridge University Press*, 1944.)

Pauling, L. "The Nature of the Chemical Bond." (*Cornell University Press*, 1942.)

Sidgwick, N. V. "The Electronic Theory of Valency." (*Oxford University Press*, 1927.)

Sugden, S. "The Parachor and Valency." (*Routledge*, 1930.)

QUESTIONS

(1) Discuss the statement that "the valency is the quotient of the atomic weight by the equivalent."

(2) Trace the development of the theory of valency.

(3) What do you understand by electrovalency, covalency, semi-polar linkages ? Give examples of compounds in which these linkages occur.

(4) What are the main differences between electrovalent and covalent compounds ? Explain them as far as possible.

(5) Give an account of the action of water on the halides.

(6) What is meant by "chelate compounds" ? Give examples.

(7) Why is it that the radical (XO_4) is of such frequent occurrence in inorganic compounds ? Show why it possesses special stability.

(8) Discuss the circumstances which gave rise to the theory of the covalency maximum. Is it possible to put forward any alternative ?

(9) Explain the occurrence of association in water ? By what means would you show that water was associated ? (See Chapter VI.)

(10) What are the characteristics of an ionising solvent ? Discuss the solubility of substances in water and in other solvents, classifying substances according to their nature and the type of solvent which dissolves them ? (See § 210.)

CHAPTER V

GASES

69. The Nature of Gases.—There is no clear dividing line between the solid and liquid state, or between the liquid and gaseous state. It is difficult to say where the one state ends and the other begins. Assuming that matter is made up of molecules, it is possible to say that in a gas the molecules have much greater freedom of motion than in either the solid or liquid state. They can move about much more easily, and can traverse greater distances without coming into collision with other molecules. This must be the case because of the pressure-volume relationships of a gas. When the pressure on a gas is doubled, the volume of the gas is reduced to one-half its previous value. Since this is possible, there must be a great deal of empty space in a gas. When the pressure on a liquid is doubled there is hardly any effect on the volume, and the same applies to a solid. In these states, then, the molecules must be much closer together than in a gas. As mentioned above, it cannot be too strongly emphasised that the three states of matter are continuous.

A gas may be defined as a substance which remains homogeneous, and of which the volume increases without limit, when the pressure on it is continuously reduced, the temperature being maintained constant.

The properties of a gas can be studied theoretically by making use of the kinetic theory of gases. In using this theory it must be remembered that certain assumptions are made which cannot be regarded as strictly correct. The theory was put forward before the structure of matter was understood, but nevertheless it has been extremely useful in explaining the properties of gases, and giving quantitative expressions of their behaviour.

70. The Kinetic Theory of Gases, and its Assumptions.—The kinetic theory assumes that a gas is made up of particles (the molecules of the atomic theory), which are moving about with random motion. The course of any particular molecule is determined entirely by probability. The molecule is supposed to be solid, spherical, and perfectly elastic. These assumptions are made principally to bring the calculations within the compass of ordinary mathematical processes. If they were not made it is doubtful

whether it would be possible to calculate anything about gases. It is now known, of course, that the molecule is not solid, or spherical, but that it is made up merely of a number of electric charges, themselves in motion, but not in disordered motion. It is important to realise, however, that the electric field associated with a molecule according to our present views, may act in such a way that the molecule behaves as if it were solid to other molecules; for when the molecule approaches another, the two fields of force interact and there is a force of repulsion, just as if two solid balls had collided.

According to the theory, the pressure exerted by a gas is due to the bombardment of the walls of the containing vessel by the molecules. Whenever a collision with the walls takes place a certain amount of momentum is given up to the walls, and this change of momentum, of course, is associated with a force (p. 184). Obviously, the collisions between molecules themselves, and between the molecules and the walls will be greater in number when the volume is decreased, for then there is less room for motion. Thus, the pressure is increased. *The average distance traversed by a molecule between one collision and the next is called the "mean free path."*

Heat is a form of energy, and when a gas is heated energy is imparted to it. It has been shown by studying the Brownian movement in gases (see Colloids, Chapter XVII.) that the mean kinetic energy of the molecules of a perfect gas (§ 72) depends only on the temperature, and not on the nature of the gas. This is of importance in studying the effect of temperature on pressure and volume of a gas.

With the aid of the assumptions made above, which must always be borne in mind, a number of laws governing the behaviour of gases can be derived.

***71. Boyle's Law.**—In order to carry out any calculations it is necessary first to realise that in a gas there is a great number of molecules, moving about with random motion, and with widely varying velocities. It would, of course, be impossible to work with conditions of this kind, so it is necessary to take an average value for the velocity. The ordinary average is not taken, but the molecules are given a velocity u, which, if they all possessed it, would make the value of the total kinetic energy, $\frac{1}{2}mnu^2$, actually what it is. In this expression m is the mass of one molecule, and n the number of molecules. This velocity u, is such that its square is equal to the mean of the squares of all the velocities possessed by the molecules, and is called the root-mean-square velocity.

Even now, we have to contend with the fact that the actual direction of motion of each molecule is not known; but use can be

made of the fact that every velocity can be resolved into three velocities at right angles, governed by the relationship,

$$u^2 = u_x^2 + u_y^2 + u_z^2,$$

where u_x, u_y, u_z, are the three components, parallel respectively to the x, y and z axes (Fig. 48).

Now, consider a cube (Fig. 49) of side l, containing n molecules, each of mass m. The root-mean-square velocity of the molecules is u. Now, from Newton's Laws of Motion,

$$P = mf,$$

where P is the force, m the mass, and f the acceleration. Now $f = \frac{du}{dt}$. Hence, $P = \frac{mdu}{dt} = \frac{d(mu)}{dt}$.

Hence force is measured by rate of change of momentum. Consider one molecule in the cube.

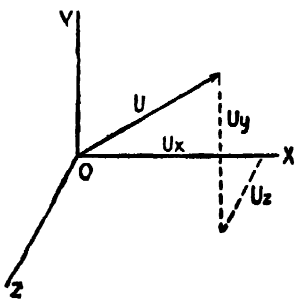


FIG. 48.

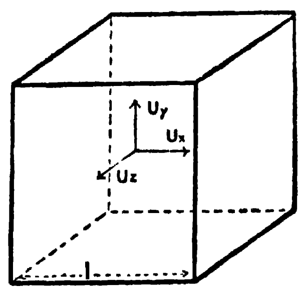


FIG. 49.

It has a root mean square velocity u, which can be resolved into three components mutually at right angles, and parallel to the edges of the cube, u_x, u_y, u_z. Consider the velocity u_x. The molecule may be supposed to be moving towards the right-hand wall. It possesses momentum mu_x when it reaches it, and since it is perfectly elastic, and the walls of the vessel are supposed to be so too, it rebounds with velocity $-u_x$, and momentum $-mu_x$.

The change in momentum is $2mu_x$. This occurs $\frac{u_x}{l}$ times per second. Hence the change in momentum for this particular component is $\frac{2mu_x^2}{l}$ per second.

Considering now the u_y component, we have, as before, the change of momentum per second $= \frac{2mu_y^2}{l}$.

Similarly for the u_z component. Hence the total change of momentum per second for all three components is

$$\frac{2mu_x^2}{l} + \frac{2mu_y^2}{l} + \frac{2mu_z^2}{l} = \frac{2mu^2}{l}$$

and, according to the statement above, this is equal to the total force over the surface of the cube.

Hence, force per unit area, *i.e.*, the pressure exerted by each molecule is given by

$$p = \frac{2mu^2}{6l^3}.$$

For the total n molecules contained in the cube, the pressure is

$$p = \frac{2mnu^2}{6l^3} = \frac{1}{3}\frac{mnu^2}{l^3}.$$

If v is the volume of the cube, $v = l^3$, and

$$pv = \frac{1}{3}mnu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At a given temperature, all the quantities on the right-hand side of this equation are constant.. Hence pv = constant.

Thus is Boyle's Law, which has been proved theoretically, by making the assumptions of the kinetic theory. Boyle's Law, however, is not followed perfectly by any gas. Since the theory indicates that it *should* be true, it is obvious that something is wrong with the theory. This inaccuracy is to be found in the assumptions made, and will be dealt with later (§§ 80, 81).

72. Gay-Lussac's or Charles's Law.—It has been proved experimentally that the mean kinetic energy of the molecules of all gases is the same at the same temperature. This conclusion is also reached theoretically. Since no particular temperature need be specified, it follows that the rate of change of the kinetic energy with temperature is the same for all gases. Expressed mathematically,

$$\frac{d(\frac{1}{2}mu^2)}{dT} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) may be written

$$pv = \tfrac{2}{3}n(\tfrac{1}{2}mu^2),$$

which on differentiation with respect to T gives

$$\frac{d(pv)}{dT} = \frac{2}{3}n\left(\frac{d(\frac{1}{2}mu^2)}{dT}\right) + \frac{2}{3}(\tfrac{1}{2}mu^2)\left(\frac{dn}{dT}\right).$$

Substituting from equation (2), we have

$$\frac{d(pv)}{dT} = n \times \text{const.} + \text{const}\frac{dn}{dT}.$$

If n is constant with respect to T—and this is true except for gases or which the molecular complexity varies with temperature—

$$\frac{d(pv)}{dT} = \text{const.}$$

In other words, the rate of change of the product of pressure and volume with the absolute temperature is constant; or, if pressure is constant, the rate of change of volume with absolute temperature is constant. This is Charles's Law, sometimes known as Gay-Lussac's Law.

* **73. Avogadro's Hypothesis.**—We can write equation (1) in the form

$$n = \frac{3}{2}\frac{pv}{(\frac{1}{2}mu^2)}.$$

Hence, if p, v and $\frac{1}{2}mu^2$ are constant, then n must be constant for all gases.

Thus Avogadro's Hypothesis, which states that equal volumes (v constant) of gases, under the same conditions of temperature ($\frac{1}{2}mu^2$ constant) and pressure (p constant), contain the same number of molecules, has a theoretical basis in the kinetic theory. Since the assumptions of the kinetic theory are not strictly accurate, Avogadro's Hypothesis is not strictly true. The method of employing it in the determination of molecular weights from gaseous densities will be discussed later (§ 82).

74. Graham's Law of Diffusion.—Graham found that a light gas would diffuse through a porous diaphragm more rapidly than a heavy gas, and also found the quantitative law governing the diffusion, which states that the rate of diffusion of a gas is inversely proportional to the square root of its density. This law can be shown to be justified on the basis of the kinetic theory.

We can rewrite equation (1) in the form

$$u^2 = \frac{3pv}{nm}.$$

Now, the density of a gas $= \frac{nm}{v} = d$ (say).

Thus

$$u^2 = \frac{3p}{d} \; ; \; u = \sqrt{\frac{3p}{d}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The reason why the light gas diffuses more rapidly through a porous diaphragm than the heavy gas has nothing to do with the size of the molecules as such. The pore of the diaphragm is, in any case, considerably larger in diameter than the largest molecule, and molecules, of whatever size, would find no difficulty in getting

through. If the pore is magnified to the size of a railway tunnel, the large and small molecules might be represented by a bird and a bee respectively. Neither would have difficulty in traversing the tunnel.

The diffusion of the molecules of a gas through a porous membrane will depend upon the velocity of the molecules, and will be directly proportional to this. Hence,

$$ku = k\sqrt{\frac{3p}{d}} = k_1\sqrt{\frac{1}{d}},$$

where k and k_1 are constants. This accounts for Graham's Law of Diffusion.

***75. Molecular Velocities.**—It is clear that equation (3) can be used directly for calculating the velocity of a molecule of any given gas. Of course, the value obtained will be the root-mean-square velocity, and not necessarily the velocity of any particular particle. It is interesting to calculate some of these velocities in order to gain an idea of the rate at which molecules move in gases. To do this, it must be remembered that if the velocities are to be found in c.g.s.u., *i.e.*, in cm. per sec., the pressure and density must also be expressed in c.g.s.u.

To calculate the root mean square velocity of the molecules of hydrogen at atmospheric pressure.

$$u = \sqrt{\frac{3p}{d}}$$

$d = 0{\cdot}00009$ gm. per c.c.
$p = 76 \times 13{\cdot}59 \times 981$ dynes per sq. cm.

$$u = \sqrt{\frac{3 \times 76 \times 13{\cdot}59 \times 981}{0{\cdot}00009}}$$

$= 183{,}800$ cms. per sec.
or 1,838 m. per sec.

TABLE XXXIII.—LIST OF MOLECULAR ROOT MEAN SQUARE VELOCITIES AT N.T.P.

Hydrogen	1,838 metres per sec.
Oxygen	460 ,,
Nitrogen	493 ,,
Argon	410 ,,
Water vapour	610 ,,
Carbon dioxide	390 ,,
Mercury vapour	180 ,,

***76. The Gas Constant.**—In text-books on heat it is shown that by

combination of the laws of Boyle and Charles, a general gas equation is arrived at of the form

$$pv = kT,$$

where k is a constant for the gas, and the other symbols have their usual significance ; k, of course, will vary with the amount of gas considered. One gram-molecule of all gases under the same conditions of temperature and pressure occupies the same volume, so the value of k will be the same for all gases if, in every instance, one gram-molecule of the gas is considered. When this is done, k is replaced by R, and the universal gas equation becomes

$$pv = RT$$

R may now be calculated. The value of R will vary according to the system of units used. If p is expressed in atmospheres, and v in litres, we obtain, as the calculation below shows, the value 0·08204 litre-atmospheres per degree.

$$p = 1 \text{ atmos.}, v = 22{\cdot}4 \text{ litres}, T = 273° \text{ Abs.}$$

$$\therefore R = pv/T = 22{\cdot}4/273 = 0{\cdot}08204 \text{ litre-atmos. per degree.}$$

If, however, p is expressed in dynes per sq. cm., and v in c.c., we obtain the value $8{\cdot}3162 \times 10^7$ ergs per degree, or 8·3162 joules per degree [1] for R. This is derived as follows :—

$$p = 76 \times 13{\cdot}59 \times 981 \text{ dynes per sq. cm.}, v = 22{,}400 \text{ c.c.},$$
$$T = 273° \text{ Abs.}$$

$$R = pv/T = \frac{76 \times 13{\cdot}59 \times 981 \times 22{,}400}{273}$$
$$= 8{\cdot}3162 \times 10^7 \text{ ergs per degree}$$
$$= 8{\cdot}3162 \text{ joules per degree.}$$

Since $4{\cdot}184 \times 10^7$ ergs = 1 gm.-calorie, $R = 1{\cdot}987$ gm.-cals. per degree, or nearly 2 gm.-cals. per degree. The last is the value most frequently used in calculations.

77. The Specific Heats of Gases.—*The specific heat of a substance is the ratio of the amount of heat required to raise the temperature of 1 gm. of it through 1° C., to that required to raise the temperature of 1 gm. of water through the same temperature range.*

It is a well-known fact that a substance has two specific heats, one measured at constant pressure, and one at constant volume. For a solid or a liquid the difference between the two is usually

[1] *Note on Units.*—The *dyne* is the force which, acting on 1 gm., produces an acceleration of 1 cm. per sec. per sec. The *erg* is the amount of work done when a body, acted upon by a force of one dyne, moves through a distance of 1 cm. in the direction of the force. One *joule* equals 10^7 ergs. The *gram-calorie* is the amount of heat required to raise the temperature of 1 gm. of water by 1° C. Observations of the mechanical equivalent of heat show that 1 gram-calorie is equivalent to $4{\cdot}184 \times 10^7$ ergs.

negligible, since the effect of heat on the volume is small. But, in the case of a gas, the expansion which takes place on heating is large, and consequently the two values of the specific heat are widely different. It is our purpose to calculate the ratio of the two specific heats for gases.

The kinetic energy of a gas molecule is proportional to its absolute temperature. From the equations

$$pv = RT$$

and

$$pv = 1/3\, mnu^2,$$

it is clear that the kinetic energy per gram-molecule of a gas ($\frac{1}{2}mnu^2$) is $3/2\, RT$.

Thus, when a gram-molecule of a gas is heated from a temperature T to a temperature $T + 1$, the increase in kinetic energy is $3/2\, R =$ 3 gm.-cals.

Thus, the molecular heat of a gas at constant volume is 3 gm.-cals., the definition of *molecular heat* being *the amount of heat required to raise the temperature of one gram-molecule of a substance through* 1° *C.* Note that this applies to *any gas*, and consequently the molecular heat of all gases at constant volume *should be* the same and equal to 3 gm.-cals.

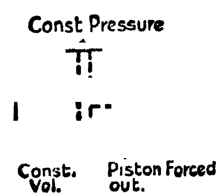


Fig. 50.

But all the energy imparted to a gas is not taken up in the form of kinetic energy, and hence all does not result in a rise in temperature. In the case of diatomic and polyatomic molecules there are many other modes of distributing the energy besides simply as energy of translation. Some of the energy may be used in causing rotation or vibration. Thus, in raising the temperature of a gas of which the molecule is complex through the same temperature range as a simple gas, more energy will have to be imparted, and the molecular heat of the gas at constant volume will then be $3 + x$ gm.-cals., where x is an unknown increase in the energy and varies from gas to gas.

If the specific heat of a gas is measured at constant pressure instead of at constant volume, a different value will be found. Suppose 1 gm. of gas is heated from 0° C. to 1° C., the volume being kept constant. The amount of heat imparted is the specific heat of the gas at constant volume. The operation may be supposed to take place in a vessel closed by a piston, the piston being kept fixed (Fig. 50).

If now, in this apparatus, there is 1 gm. of gas at 0° C., and it is heated to 1° C., the piston being free, the piston will be forced out

against the pressure of the atmosphere. The amount of heat imparted is the specific heat of the gas at constant pressure. In this case, the gas has done a certain amount of external work. It has pushed out the piston. The energy required to do this must come from the heat imparted, as there is no other source. The heat taken up by the gas at constant pressure is used partly to raise the temperature of the gas, and partly to provide the energy for the external work done. Therefore, to raise the temperature of the gas through 1° C. at constant pressure more heat must be applied than to bring about the same increase in temperature at constant volume, because part of the heat is, in the first instance, used in the performance of external work. The amount of the work done and heat used may be calculated.

Suppose we have a volume of gas v_1 and it expands to a volume v_2 at constant pressure p. Consider a small volume change dv. The work done will be pdv. The total work done over the whole volume change will be given by integrating pdv between the limits v_1 and v_2.

$$\int_{v_1}^{v_2} pdv = p(v_2 - v_1) = \text{pressure} \times \text{change in volume.}$$
$$= R(T_2 - T_1) = R \text{ (for } T_2 - T_1 \doteq 1)$$
$$= 2 \text{ gm.-cals.}$$

The molecular heat at constant pressure is therefore greater than that at constant volume by 2 gm.-cals. Hence,

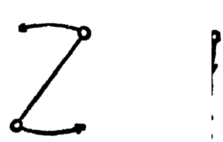
$$C_p - C_v = R.$$

If the molecular heat at constant volume is $3 + x$ gm.-cals., that at constant pressure will be $5 + x$ gm.-cals., and the ratio of the specific heats will be $(5 + x)/(3 + x)$. The symbols for specific heats at constant pressure and constant volume are C_p and C_v, and for their ratio, γ. Thus

$$\gamma = C_p/C_v = (5 + x)/(3 + x).$$

If $\quad x = 0, C_p/C_v = 5/3 = 1{\cdot}667.$

This result may be expected only in the case of very simple



(a) Rotation. (b) Vibration.

molecules, and it is actually found for monatomic gases and vapours. Thus the ratio of the specific heats of the inert gases is 1·67. As the

molecule becomes more complex, so the value of x increases. When we have a diatomic molecule, there is a possibility of a rotational and a vibrational motion, as well as direct translation.

For most diatomic gases, it is found that $x = 2$, in which case, $C_p/C_v = 7/5 = 1{\cdot}40$.

For triatomic gases, $x = 3$, and hence $C_p/C_v = 8/6 = 1{\cdot}33$.

The following table will indicate how closely the ratio of the specific heats approximates to one or other of these numbers.

TABLE XXXIV.—RATIO OF SPECIFIC HEATS OF GASES AT 15° C.

Helium	1·666
Argon	1·67
Hydrogen	1·408
Oxygen	1·396
Nitrogen	1·405
Air	1·403
Carbon monoxide	1·404
Hydrogen chloride	1·400
Chlorine	1·355
Carbon dioxide	1·302
Nitrous oxide	1·300
Sulphur dioxide	1·285
Sulphuretted hydrogen	1·340
Steam (100° C.)	1·306
Ammonia	1·310
Acetylene	1·280
Methane	1·310
Ethylene	1·250

It must be borne in mind that the explanation of the value of x in the above work is not yet definitely established. However, the usual explanation is based upon the principle of equipartition of energy, which was deduced by Maxwell and Boltzmann. According to this principle, the energy imparted to a gas will be equally distributed between every degree of freedom. A degree of freedom is every possible mode of motion of a molecule.

Thus, in the case of a monatomic gas, the only type of motion possible is motion in a straight line, or motion that can be made up of small motions in a straight line. This motion can, however, be represented by three components mutually at right angles. The system therefore has three degrees of freedom. The kinetic energy of a molecule is $1/2\ mu^2$, and this can be resolved into the three components, connected by

$$\tfrac{1}{2} mu^2 = \tfrac{1}{2} mu_x^2 + \tfrac{1}{2} mu_y^2 + \tfrac{1}{2} mu_z^2.$$

Now, according to the theory of equipartition of energy,

$$\tfrac{1}{2} mu_x^2 = \tfrac{1}{2} mu_y^2 = \tfrac{1}{2} mu_z^2 = \tfrac{1}{2} RT.$$

Every degree of freedom of this motion is therefore associated with an amount of energy $= 1/2\ RT$ per gram-molecule. The total energy is $3/2\ RT$, and the corresponding heat capacity, $3/2\ R$ cals. Gases of all kinds have translatory motion, and therefore they all have energy $3/2\ RT$ corresponding to this motion, as well as any extra due to other types.

As has already been mentioned, a gas which has molecules made up of more than one atom may possess vibrational energy, which is both potential and kinetic. For a diatomic molecule this motion can only exist in one direction, *viz.*, along the axis of the molecule, and hence two degrees of freedom would be assigned to it, one for potential and one for kinetic energy. For a triatomic gas, such motion could, in general, take place along three directions—the sides of the triangle formed by joining up the centres of the atoms. In this case, then, there would be six vibrational degrees of freedom.

Consider now rotational motion. Molecules will rotate about their centre of gravity as a result of collisions with other molecules. Such motion is described in a plane, and is resolvable into two components, each of which would be assigned one degree of freedom. This assumes that the molecule is diatomic ; or if polyatomic, the atoms must be arranged linearly. In the case of a triatomic gas where the atoms stand at the corners of a triangle, it might be expected that three degrees of freedom would result.

For a diatomic gas, then, we have three degrees of freedom for translation, two for rotation and two for vibration. If we assume the molecule to be rigid, the last two are lost, and so the energy is now $\frac{5}{2} RT$, or the gas has a molecular heat capacity of 5 cals. per degree. This seems to be true for most diatomic gases, but it is possible, according to the theory, for a diatomic gas to possess seven degrees of freedom, and it would then have a molecular heat capacity of 7 cals. per degree.

78. The Determination of the Ratio of the Specific Heats of Gases.—Obviously this could be carried out by measuring the specific heat at constant pressure and at constant volume, and calculating their ratio, but, in addition, there are some indirect methods.

The direct determination of the specific heats of gases is a matter of some difficulty, since the volume of a given mass of gas is so large. Large volumes of gas have to be used if good results are to be obtained.

(*a*) *Direct Determination of C_p.*—This can be carried out by a

modification of the method of mixture applied to the ordinary determination of the specific heat of a solid. The method, which was used by Regnault and others, consists in passing a known volume of gas heated to a definite temperature through a calorimeter containing cold water, and measuring the amount of heat liberated.

The continuous flow method of Callendar has also been used. The gas, heated to a definite temperature, is passed into a special form of continuous flow calorimeter, and is then heated electrically. The rise in temperature is measured by means of a platinum resistance thermometer. The method has been applied by Scheel and Heuse for low temperature determinations of C_p.

McCollum used a modification of Regnault's method to determine

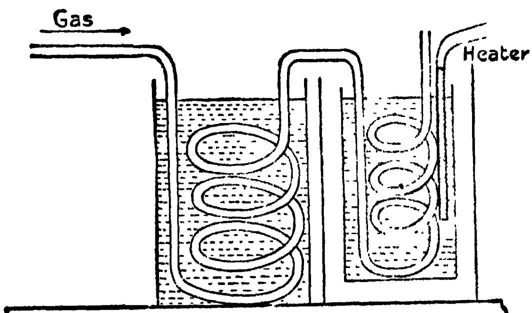


FIG. 51.—McCollum's Apparatus for determining the Specific Heat of Nitrogen Tetroxide at Constant Pressure.

the specific heat of nitrogen tetroxide at constant pressure. The gas was passed through a spiral tube in a thermostat, the time taken for the gas to pass through the tube being sufficiently long to ensure that it attained the temperature of the bath. It then passed into a slightly warmer bath, the temperature of which was kept constant by an electric heater. The current flowing in the latter was measured. When the cool gas passed into the warmer vessel, it tended, of course, to cool it. Additional current had to be passed through the heater to maintain the bath at constant temperature. The amount of this extra current was a measure of the heat absorbed by the gas. Let the mass of gas passing through the bath in 1 sec. be m gms. If the additional current flowing through the heater is I amperes, and its resistance is R ohms, then, in 1 sec. the amount of heat given out by the heater is $H = \frac{I^2R}{4\cdot184}$ calories. This is the amount of heat taken up by the mass of gas m, in raising its temperature from $t°$ C. (the temperature of the thermostat) to $t_1°$ C.

(the temperature of the bath). If C_p is the specific heat of the gas at constant pressure,

$$m\,C_p\,(t_1 - t) = \frac{I^2R}{4{\cdot}184}$$

$$C_p = \frac{I^2R}{4{\cdot}184m\,(t_1 - t)}.$$

(*b*) *Direct Determination of* C_v.—This is a somewhat more difficult operation. Joly used his steam calorimeter for this purpose (Fig. 52). This instrument consists of two thin copper spheres supported from the ends of a balance beam, and surrounded by a chamber which can be filled with steam. The two spheres should balance each other, and when steam is admitted into the chamber it will condense on the two spheres in equal amount, and hence they will still weigh the same. The spheres are first evacuated, and then one of them is filled with the gas to be investigated, under pressure. The steam is admitted, and it is now found that a different quantity of steam condenses on the sphere containing the gas from that condensing on the evacuated one. The difference is found by adding weights. The difference in the amount of steam condensed is due to the different heat capacities of the globes, and from the experimental results it is easy to calculate the specific heat of the gas.

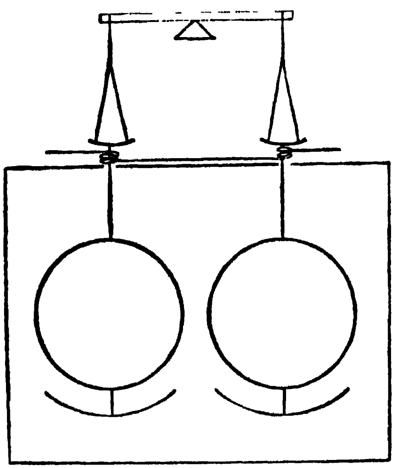


Fig. 52.—The Joly Steam Calorimeter.

The method has been modified by Eucken for work at low temperatures, and its accuracy has been considerably improved.

The explosion method, originated by Bunsen, and more recently modified by Pier, is rather interesting, and is capable of yielding fairly accurate results. The principle of the method is as follows: A gas that will explode with oxygen is admitted with the latter, and mixed with various indifferent gases, into a closed vessel. The mixture is exploded, and the maximum pressure reached is measured. From this the temperature to which the mixture has been heated can be calculated. Knowing the heat of the reaction (Chapter XV.), and the heat capacity of the vessel, the heat capacity of the gas can

be obtained. Pier used a special form of manometer, involving the use of a very thin steel plate, with a high period of vibration. The plate was deformed by the pressure increase due to the explosion, and the deformation was measured photographically, and compared with that produced by known pressures.

(c) *Indirect Methods of Determining C_p/C_v.*—(1) ***The Method of Clément and Desormes*** (1819).—To understand this method, it is necessary to be acquainted with the definition of an adiabatic change. ***An adiabatic change is one in which no heat is allowed to escape from, or be added to, the system during the change.*** The temperature in an adiabatic change must, then, alter. It is here that it differs from an isothermal change in which there is no alteration in temperature.

In the Clément and Desormes' method, a large vessel is filled with the gas under observation to a pressure a little above atmospheric. This pressure is measured by means of a manometer attached to the vessel. The vessel is then opened for a very short while, during which the gas inside attains atmospheric pressure, and, in so doing, expands and cools a little. When the vessel is closed, the gas begins to attain room temperature again, and so its pressure again increases. The increase is measured.

In considering the theory of this experiment we may derive first the equation connecting the pressure and volume of a gas which undergoes adiabatic expansion. Consider one gram-molecule of a gas, and allow it to expand adiabatically from a volume V to $V + dV$, under constant pressure P. The work done is PdV. Suppose the temperature falls by dT. The amount of energy corresponding to the external work done is, therefore, $-C_vdT$, where C_v is the molecular heat at constant volume.

Hence $$PdV = -C_vdT.$$

But $$PV = RT,$$

$$\therefore R \cdot \frac{dV}{V} = -C_v \cdot \frac{dT}{T}.$$

Considering a volume change from V_1 to V_2, the temperature falls from T_1 to T_2. Hence

$$\int_{V_1}^{V_2} R \cdot \frac{dV}{V} = -\int_{T_1}^{T_2} C_v \frac{dT}{T}.$$

$$\therefore R \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1}.$$

But $$C_p - C_v = R \qquad (\S\ 77)$$

$$\therefore (C_p - C_v) \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1},$$

or
$$\log_e \frac{T_2}{T_1} = (\gamma - 1) \log_e \frac{V_1}{V_2},$$

or
$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}.$$

Since
$$P_1V_1 = RT_1 \text{ and } P_2V_2 = RT_2,$$
$$P_1V_1^\gamma = P_2V_2^\gamma = \text{constant}.$$

and
$$P_1^{1-\gamma}T_1^\gamma = P_2^{1-\gamma}T_2^\gamma = \text{constant}$$

Generally, the equations may be written
$$PV^\gamma = \text{constant}.$$
$$P^{1-\gamma}T^\gamma = \text{constant}.$$
$$TV^{\gamma-1} = \text{constant}.$$

This may now be applied to the conditions obtaining in the Clément and Desormes' experiment. Suppose the original pressure of the gas is P_1, and atmospheric pressure is P. Let the final pressure be P_2. Let T be the initial temperature, and t the decrease in temperature. Then, whilst the temperature of the gas rises from $T - t$ to T, its pressure increases from P to P_2. Hence
$$\frac{P}{P_2} = \frac{T-t}{T}.$$

From the adiabatic equation given above,
$$P_1^{1-\gamma}T^\gamma = P^{1-\gamma}(T-t)^\gamma$$
$$\therefore \left(\frac{P_1}{P}\right)^{1-\gamma} = \left(\frac{T-t}{T}\right)^\gamma = \left(\frac{P}{P_2}\right)^\gamma$$

Taking logarithms of both sides of the equation,
$$(1-\gamma)\log_e\left(\frac{P_1}{P}\right) = \gamma \log_e\left(\frac{P}{P_2}\right),$$
$$\therefore \gamma\left(\log_e \frac{P}{P_2} + \log_e \frac{P_1}{P}\right) = \log_e \frac{P_1}{P},$$
$$\therefore \gamma = \frac{\log_e \dfrac{P_1}{P}}{\log_e \dfrac{P}{P_2} + \log_e \dfrac{P_1}{P}} = \frac{\log_e P_1 - \log_e P}{\log_e P_1 - \log_e P_2}.$$

Hence γ can be determined by observations of the pressures P_1, P_2 and P. No determination of temperature is necessary.

Lummer and Pringsheim (1898) have improved the accuracy of this method by employing a very large vessel (90 litres capacity), and allowing the excess pressure to blow off through a large orifice.

This made certain that the gas had actually reached atmospheric pressure. The temperature of the gas was determined immediately by means of a platinum resistance thermometer placed at the centre of the flask. Since the process is adiabatic, the formula to use is :—

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}$$

where T_1, P_1 are initial temperature and pressure, and T_2, P_2 are the corresponding final conditions.

(2) *By Determining the Velocity of Sound.*—It was at first thought

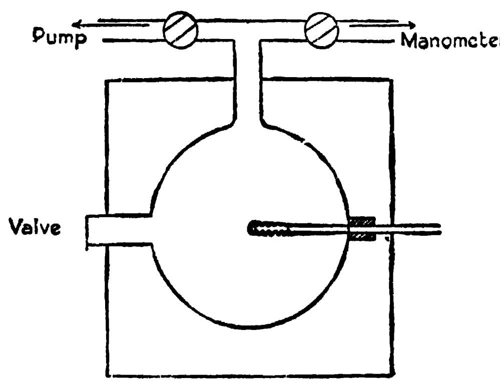


FIG. 53.—Lummer and Pringsheim's Modification of Clément and Desormes' Apparatus (diagrammatic).

that the velocity, v, of sound in a gas was connected with its elasticity under isothermal compression, E, and its density, d, by the expression

$$v = \sqrt{\frac{E}{d}}.$$

Later it was found that the elasticity to be used was not that under isothermal compression, but that under adiabatic compression, E_a; for when a sound wave passes through a gas there is no time for the heat to be dissipated before the next pulse follows, so that the whole process is adiabatic. The velocity of sound in a gas is therefore given by

$$v = \sqrt{\frac{E_a}{d}}.$$

Now, E_a is related to E by the expression

$$\frac{E_a}{E} = \gamma = \frac{C_p}{C_v},$$

and E is identical with the pressure of the gas, p, so we have

$$E_a = p\gamma \text{ and } v = \sqrt{\frac{\gamma p}{d}}.$$

If now we have two gases of density d_1 and d_2 under the same pressure, the velocity of sound in the gases being v_1 and v_2, respectively, and the ratio of the specific heats for the two gases γ_1 and γ_2, we have

$$v_1 = \sqrt{\frac{\gamma_1 p}{d_1}} \qquad v_2 = \sqrt{\frac{\gamma_2 p}{d_2}}$$

$$\therefore \frac{v_1^2}{v_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1}.$$

Now, the velocity of a wave motion is connected with the wavelength λ, and frequency n, by the expression $v = n\lambda$.

If symbols with the suffixes 1 and 2 refer to the two gases, for a note of the same frequency, n,

$$v_1 = n\lambda_1 \qquad v_2 = n\lambda_2$$

$$\therefore \frac{v_1}{v_2} = \frac{n\lambda_1}{n\lambda_2} = \frac{\lambda_1}{\lambda_2} \qquad \therefore \frac{\lambda_1^2}{\lambda_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1}.$$

Hence,

$$\frac{\gamma_1}{\gamma_2} = \frac{\lambda_1^2 d_1}{\lambda_2^2 d_2} \quad \ldots\ldots\ldots \quad (i)$$

Two practical methods are possible. Either the actual velocity of sound in a gas may be found, or the wavelength of the note of a

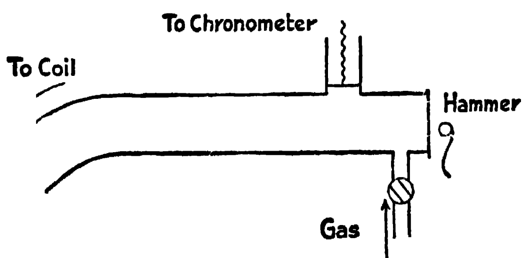


FIG. 54.—Dixon's Apparatus.

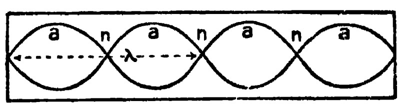
given frequency may be determined. Until comparatively recently it has not been possible to carry out the first experiment because with the older methods such large quantities of gas were required. However, in 1921, Dixon determined the velocity of sound in certain gases directly, and in some cases over a considerable range of temperature. He first showed that the velocity of sound was the same in coiled tubes as in straight ones. He then sent sound waves through gases in coiled tubes, about 15 metres in length and 25 mm.

in diameter. The sound wave was started by a hammer worked like an electric bell hammer, striking a steel diaphragm at the end of the tube. When the wave passed the platinum disc, a mark was made by a self-recording chronometric apparatus, and a similar piece of apparatus marked its arrival at the other end. In this way the time taken for the wave to travel the length of the tube was found. After correcting for the fact that the velocity of sound in tubes is not quite the same as that in the open, the velocity was calculated.

The value of γ could then be found from the equation

$$= \sqrt{\frac{\gamma p}{d}},$$

but Dixon used, instead of the density d of the gas, the expression



n = nodes ; a = antinodes ; $nn = \lambda/2$.

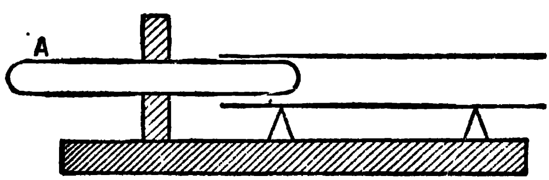


FIG. 55.—Behn and Geiger's modification of Kundt's method.

for the density from the molecular weight of the gas given by Daniel Berthelot (§ 81), giving as the final relationship

$$\gamma = \frac{v^2 M}{RT}\left[1 + \frac{9p}{128p_c} \cdot \frac{T}{T_c}\left(1 - 6\frac{T^2}{T_c^2}\right)\right],$$

where M is the molecular weight of the gas, R the gas constant, T the absolute temperature of measurement, T_c the critical temperature, and p_c the critical pressure.

The following results were obtained :—

	γ
Nitrogen	1·408
Carbon dioxide	1·296
Methane	1·301

The second method mentioned is rather more convenient. In this the wavelengths of notes of the same frequency passed through two gases are compared. The apparatus is called Kundt's tube,

although the modification described below has been devised by Behn and Geiger. The gas under test is placed in the dried sealed tube A, together with some lycopodium powder, or silica dust. The tube is clamped at its middle, and small discs of lead can be fixed to either end so that the tube may be made to vibrate. One end of the tube enters a wider, open tube, containing air and some lycopodium or silica dust. The sealed tube is stroked with a wet cloth, which sets it into vibration, and the air in the wider tube is also set into vibration by resonance. The powder in the tubes becomes heaped up at the places of least motion, *i.e.*, at the nodes. The distance between two heaps will therefore be half a wavelength (Fig. 55). By measuring the distances, and multiplying by two, the wavelength of sounds of the same frequency in the gas and in air can be obtained.

The ratio of γ_1 to γ_2 for the two gases can be obtained by using the formula (1) on p. 198, the density of the gases being known. If γ is known for one of them, the value for the other can readily be calculated. It should be noted that this is essentially a comparative method. This method was used by Ramsay and others in finding the ratio of the specific heats of the inert gases, although a slightly different apparatus was used. It is a little difficult to work with helium as, owing to its lightness, it does not give good dust heaps.

79. The Determination and Calculation of some Molecular Constants.—(*a*) *The Mean Free Path.*—The mean free path has already been defined as the mean distance through which a molecule can move without coming into collision with another. Of course, the actual distance through which a molecule moves before collision varies enormously from time to time. Sometimes it may travel a long distance before meeting another molecule, especially if the gas is under reduced pressure. At other times only a fraction of the mean free path is traversed. The viscosity of a gas will obviously be directly connected with the mean free path. The ***coefficient of viscosity***, η, is defined as *the force per unit area exerted between two parallel layers at unit distance apart, when the velocity of streaming differs by unity in the two layers.*

From the kinetic theory it may be shown that

$$\eta = \tfrac{1}{3} d\lambda u$$

where λ is the mean free path, d is the density, and u the root-mean-square velocity.

If we substitute the value of u obtained in § 74,

$$u = \sqrt{\frac{3p}{d}}$$

in this equation, the expression

$$\lambda = \eta\sqrt{\frac{3}{pd}}$$

is obtained.

As would be expected, the mean free path is greater the lower is the pressure. The value of the mean free path can therefore be obtained from observations of viscosity.

The collision frequency, which is given by $\frac{u}{\lambda}$, can also be obtained quite easily.

It will be seen from Table XXXV. that the mean free path of oxygen at N.T.P. is of the order of 10^{-5} cm. It is twice this in hydrogen. For comparison, the average wavelength of light in the visible spectrum is 5×10^{-5} cm. At low pressures the mean free path may amount to several centimetres.

In 1 second, a molecule describes as many free paths as it makes collisions, and hence the sum of the free paths is equal to the mean speed. Taking the case of hydrogen, the root-mean-square velocity, u, is 183,800 cm. per second, and the mean free path is $17{\cdot}8 \times 10^{-6}$ cm. Hence the number of collisions per second is

$$\frac{u}{\lambda} = \frac{183{,}800}{17{\cdot}8 \times 10^{-6}} = 10{,}330 \times 10^{6}.$$

It need not be pointed out that this number is very large. It might be noted, however, that even when the mean free path is increased to 1 cm., which could happen at very low pressures, the number of collisions per second is still 183,800, *i.e.*, nearly 200,000 per second.

TABLE XXXV.—MEAN FREE PATHS (AT N.T.P.)

Hydrogen	$17{\cdot}8 \times 10^{-6}$ cm.
Oxygen	$10{\cdot}0 \times 10^{-6}$
Nitrogen	$9{\cdot}5 \times 10^{-6}$
Carbon dioxide	$6{\cdot}3 \times 10^{-6}$
Carbon monoxide	$9{\cdot}3 \times 10^{-6}$
Water vapour	$7{\cdot}2 \times 10^{-6}$

(*b*) *Avogadro's Number.*—Avogadro's Law states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules. It is interesting to know how many molecules there are in a gram-molecule of a gas. This should be the same for all gases, and is called Avogadro's number, N. Occasionally, we meet with the number of molecules contained in 1 c.c. of gas at N.T.P. This is called Loschmidt's

number, and is denoted by n. It is obvious that

$$N = 22,414n,$$

since one gram-molecule of a gas occupies a volume of 22,414 c.c.

Avogadro's number can be determined by a variety of experimental methods, which give surprisingly concordant results. A few of these methods are described.

(1) *The Method of Rutherford and Geiger.*—The element radium is continually shooting out charged helium atoms, called α-particles (Chapter II., § 21). They move very rapidly, in fact, about 100,000 times as fast as an ordinary gas molecule. They possess the property of causing zinc sulphide to glow when they fall upon it. If, then, the α-particles are not shot off too frequently it is possible to count them, since every time they impinge on a zinc sulphide screen they cause a flash. The apparatus for counting the α-particles is shown in the figure (56) and is called a spinthariscope.

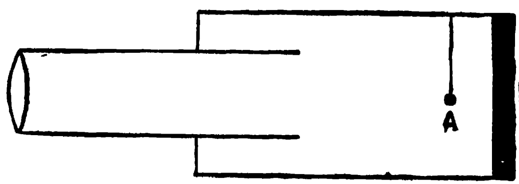


FIG. 56.—Spinthariscope (diagrammatic).

The radium preparation A, was hung in front of the zinc sulphide screen B, which was viewed through a lens. A separate experiment was carried out to find out how much helium was formed from a larger, known amount of radium, in a given time. The volume of the gas and the number of atoms in it were known, because they had been directly counted as α-particles. Hence the number of atoms (of helium ; molecules of any other gas) in 1 c.c. could be calculated, and from this Avogadro's number could be obtained. Allowance was made for the fact that only a fraction of the α-particles strike the screen. The results obtained for the experiments were :—

$$\text{Number of molecules per c.c.} = 2{\cdot}7 \times 10^{19}$$
$$\text{Avogadro's number} = 6{\cdot}05 \times 10^{23}$$

The method was improved in 1908, the apparatus depicted in the figure (57) being used. A long glass tube, TT, 450 cm. long, and 2·5 cm. wide, called the firing tube, was exhausted, and a radium preparation on a lead plate was placed at A. Some α-rays shot along the tube, passed through the narrow tube B, and passed into the ionisation chamber C, through the window F. The gas in the ionisation chamber, which was at low pressure, became ionised every

time an α-particle passed into it, and this rendered the gas conducting. A current then passed through the electrometer (which was connected to the wire w, and the outside of the chamber), every time the gas was ionised. It was thus possible to count the α-particles, and knowing the volume of helium produced in a given time, obtained by a separate experiment, Avogadro's number could be found. The value obtained was

$$N = 6{\cdot}14 \times 10^{23}.$$

Allowance was made for the fact that only a fraction of the α-particles got into the ionisation chamber. It may be noted that in the spinthariscope method the minutest quantity of radium is used, whereas the second method requires an appreciable quantity.

(2) *Perrin's Method.*—This is based on a study of the Brownian Movement (Chapter XVII.). If very fine particles are suspended in

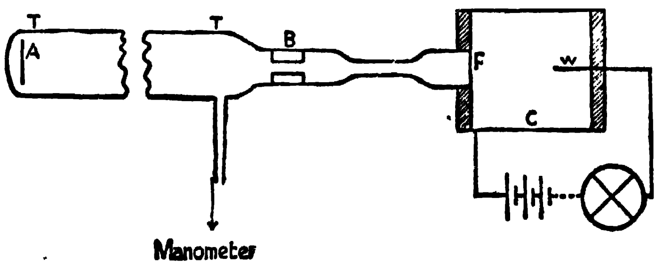


FIG. 57.—Rutherford and Geiger's Apparatus (diagrammatic).

a liquid and are examined under the ultramicroscope, it is found that they are moving about rapidly and with random motion. This motion is called the Brownian Movement, because it was first observed by the botanist Brown, with pollen grains. The reason why the particles are moving about in all directions is because they are continually being bombarded by molecules of the medium in which they are placed. This bombardment will affect them differently from time to time, for at one instant they may be hit by many or rapidly moving molecules, and at other times by few or slowly moving molecules. Hence their motion is continually varying. Perrin supposed that a particle suspended in a liquid would behave just like a large molecule and would possess the same mean kinetic energy as a molecule of the liquid. He calculated the way in which gravity should cause an alteration in the numerical density of these particles in a column of fluid. Owing to their weight, there will be a larger number at the bottom than elsewhere, and this number will get smaller and smaller as we go up the column. Two effects have

to be taken into account. The first is gravity, which causes a downward motion, and the second is osmotic pressure causing a diffusion upwards (Chapter XI.). Perrin obtained the following expression :—

$$\frac{2}{3} w \log \frac{n_0}{n} = \phi (D - \delta) g h,$$

where w is the mean kinetic energy of the particle ; n_0 and n the average number of particles per unit volume at levels which differ in height by h ; ϕ the volume of a particle ; D and δ the densities of the particle and the liquid respectively. Perrin set out to determine w experimentally, making use of this expression, and it will be seen that in order to do so it is necessary to determine the volume of a particle, and the numbers present at given heights in the medium. The volume of the particle was found by counting the number in a given volume of suspension, which was then evaporated to dryness, and the weight of the remaining particles determined. The weight of one particle could thus be found, and knowing the density of the particle (which was assumed by Perrin to be the same in the particle as in the bulk condition, though it need not necessarily be), the volume could be calculated. The number of particles at different levels was obtained by focussing a microscope on a certain level and counting the number, and then turning the focussing screw so as to raise the objective through a given distance. This would now be focussed on a new layer, at a distance from the previous one equal to the distance through which the microscope had been raised. The number of particles in the newly focussed layer was then counted. w can thus be calculated.

We have already seen (§ 73) that the mean kinetic energy of a molecule is given by

$$w = 3pv/2n.$$

For a gram-molecule of a gas, which contains N molecules,

$$pv = RT.$$

Hence

$$w = 3RT/2N.$$

Knowing w, N can be found.

The value obtained by this method was

$$N = 6{\cdot}90 \times 10^{23},$$

which is in very good agreement with the Rutherford and Geiger value.

(3) *The Millikan Oil-Drop Method.*—This method, which has already been described in connection with the determination of the charge of the electron, can be utilised to furnish a value for

Avogadro's number by using the relationship that the number of electrons in one gram-molecule of ions is N, and if e is the charge on one, and F the Faraday, then $Ne = F$ (§ 26).

F is readily found by electrolysis experiments; e is found by Millikan's method, as previously described, to be $1{\cdot}59 \times 10^{-19}$ coulombs; hence $N = 6{\cdot}062 \times 10^{23}$, if $F = 96{,}500$ coulombs. This is probably the most accurate method of determining N.

Quite a number of methods have been used to determine Avogadro's number, and all give concordant results, some of which are given in the table below. This fact alone shows that there can be no doubt about the existence of molecules.

TABLE XXXVI.—VALUES OF N

Classical kinetic theory . .	10×10^{23} (approx.)
Brownian movement (Perrin) .	$6{\cdot}90 \times 10^{23}$
Radiant heat	$6{\cdot}19 \times 10^{23}$
Counting α-particles . .	$6{\cdot}14 \times 10^{23}$
Electronic charge (Millikan) .	$6{\cdot}06 \times 10^{23}$
Brownian movement (Nordlund)	$5{\cdot}90 \times 10^{23}$

(c) *The Mass of the Molecule.*—Knowing Avogadro's number, we can calculate the mean mass of the molecules, if the gram-molecular weight of the gas is known. Thus, for oxygen, the gram-molecular weight is 32. Hence the mass of the oxygen molecule is

$$\frac{32}{6{\cdot}06 \times 10^{23}} = 5{\cdot}28 \times 10^{-23} \text{ gm.}$$

The mass of the hydrogen atom calculated in a similar way is $1{\cdot}663 \times 10^{-24}$ gms.

***80. Deviations from Boyle's Law.**—Boyle's experiments were carried out within a comparatively small pressure range, and were not sufficiently accurate to show whether the law was strictly correct or not. In fact, if such data were obtained from experimental work in these days, observers would be chary of deducing a law from them. At the beginning of the nineteenth century many people attempted to verify the law, but the best work was done by Regnault in 1847.

He improved the apparatus so as to reduce the experimental error, and also increased the pressure range up to 27 atmospheres. He found that the gases he used, hydrogen, nitrogen, air and carbon dioxide, did not obey the law perfectly. Hydrogen was found to be less compressible, and the other gases more compressible, than the law demands.

The work of Regnault was improved upon by Amagat, who

carried out experiments first up to a pressure of 400 atmospheres, using a mercury manometer. For this purpose, the mercury tube was placed in the shaft of a coal mine. By using a sort of hydraulic press, he was able in a later series of experiments to reach 3,000 atmospheres.

The results of these experiments showed that no gas strictly obeys Boyle's Law. Gases are therefore not perfect, a perfect gas being defined as one which obeys Boyle's Law. The nature of the deviations are best shown by plotting the product of pressure and volume against pressure. If a gas obeyed Boyle's Law this curve would be a straight line, the line AB in Fig. 58.

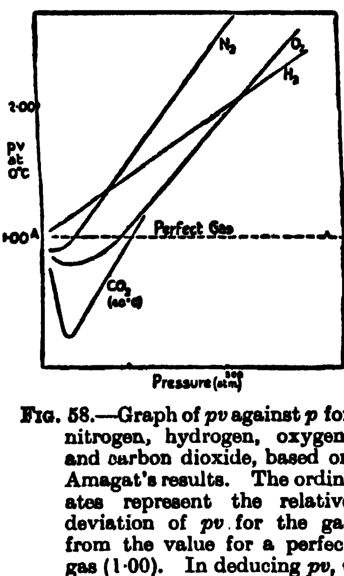


Fig. 58.—Graph of pv against p for nitrogen, hydrogen, oxygen, and carbon dioxide, based on Amagat's results. The ordinates represent the relative deviation of pv for the gas from the value for a perfect gas (1·00). In deducing pv, v is taken as 1, when $p = 1$ atmosphere.

It will be noticed that the curve for hydrogen starts ascending at once, whilst for the others the curves all show a decrease in pv at first. Ultimately, all gases behave like hydrogen, above, say, about 400 atmospheres. It has been shown that the inert gases give curves exactly like that of hydrogen. The gases which are most easily liquefied deviate the most from Boyle's Law.

Experiments on gases at low pressures have not yet shown definitely whether gases deviate from the law at extremely low pressures.

81. Modifications of Boyle's Law.—The fact that experiment reveals deviations on the part of most gases from Boyle's Law must be explicable on a theoretical basis. Boyle's Law has been derived in a previous section (§ 71) from the kinetic theory. It is possible that the assumptions upon which the kinetic theory is based are at fault.

It will be remembered that in deriving Boyle's Law certain assumptions were made about the size, shape and properties of molecules. In the derivation, it was tacitly assumed that the molecules had a negligible volume, and that there were no attractive forces between them. Both these assumptions are, of course, not true at ordinary temperatures and pressures. When the pressure of a gas is considerably reduced the volume occupied by the molecules

may be negligible when compared with the space in which they move, but not under ordinary conditions.

In 1865, Hirn put forward an equation which took the first of these corrections into account. If the molecules do occupy some volume, then the space available for their motion must be reduced, and so, in the ordinary Boyle's Law equation, $pv = RT$, we must substitute for v, $(v - b)$, where b is a quantity dependent upon the volume occupied by the molecules. It is not a difficult mathematical exercise to show that it should correspond to four times the volume of the molecules.

A correction was also attempted for the second error, the attractive force exerted by the molecules on each other. That such an attractive force exists is shown by the Joule-Thomson effect (Chapter VI., § 89). For a molecule in the centre of the gas the attraction of other molecules will, on the average, be spread over a sphere uniformly, and so need not be taken into account for our purpose. Molecules near the edges will, however, experience an attractive force which tends to drag them inwards, and so the velocity with which they strike the walls, and the corresponding pressure, will be lower. Thus the observed pressure is less than that which would be exerted if there were no attractive force. Hirn therefore proposed to add a pressure, P_i to p, in order to increase the pressure to the value it would have if there were no attraction. P_i was called the intrinsic pressure, or the internal pressure of the gas.

Hirn's modification of Boyle's Law therefore reads :—

$$(p + P_i)(v - b) = RT.$$

Van der Waals (1873) carried the matter further. He added a factor $\frac{a}{v^2}$ to the pressure to account for the attraction of the molecules for each other. The correction will depend upon (i.) the number of molecules in the surface layer, and (ii.) the number of molecules in the interior. Both these numbers are proportional to the density *i.e.* (for a given mass of gas), inversely proportional to the volume. Hence the form of the correction. Van der Waals' equation is therefore

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

The equation of van der Waals correctly explains the general behaviour of gases, and, incidentally, also of liquids, throughout the whole range of temperatures and pressures, but quantitative agreement with experimental data is still not quite exact. Hence, many equations, most of them empirical, have been put forward to cover the experimental facts. It would be useless to consider all of them,

as well over a hundred modifications of van der Waals' equation have been proposed. The most important of them are the equations of Dieterici, of Clausius, and of Berthelot. Dieterici made allowance for the density gradient at the boundary of the gas as the internal pressure diminishes to zero. The equation is

$$p\,(v - b) = RTe^{-\frac{a}{RT}},$$

where e is the base of natural logarithms.

Over small ranges of pressure, Dieterici's equation agrees with that of van der Waals, but at high pressures the differences become quite appreciable, and, in general, Dieterici's equation explains the experimental facts better.

It was at first thought that the a factor in van der Waals' equation was independent of temperature. Amagat's work on carbon dioxide showed that this was not so, and Clausius modified van der Waals' equation accordingly, by putting the term $a/[T(v + c)^2]$ for a/v^2. The Clausius equation is therefore

$$\left(p + \frac{a}{T(v + c)^2}\right)(v - b) = RT.$$

It explains the relationship between pressure, temperature and volume reasonably well for some gases, but its success is not general.

The equation of Daniel Berthelot depends upon the critical constants of the gas concerned. As explained in the next chapter, the van der Waals' constants a and b have been found to bear a relationship to the critical constants of a gas (Chapter VI., § 87). Berthelot derived an empirical relationship between the constants a and b, and the critical constants, and substituted their values in the van der Waals' equation, obtaining the equation

$$pv = NRT\left[1 + \frac{9}{128}\frac{p}{p_c}\cdot\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

where p_c and T_c are the critical pressure and temperature, respectively.

Berthelot's equation gives very accurate agreement between observed and calculated values, but it must be remembered that it applies only to a pure gas, *i.e.*, to a gas consisting of a single species of molecules only. The equation gives good results in the neighbourhood of the critical point, when others fail. It can be applied to saturated vapours.

82. Deviations from the other Gas Laws.—(*a*) *Avogadro's Hypothesis.*—Just as there are deviations from Boyle's Law, so the other gas laws are found to be not strictly accurate. It will be remembered that Avogadro's Hypothesis was derived on the basis of the

kinetic theory from the result obtained for Boyle's Law (§ 73). If the latter is wrong, being based on wrong assumptions, it follows that the former must be wrong also. This is indeed the case. Equal volumes of gases under the same conditions of temperature and pressure do not contain the same number of molecules, and the usual statement of Avogadro's Hypothesis is probably only valid at very low pressures where the gases probably behave as perfect gases, and where Boyle's Law itself may be obeyed.

It follows from this that the usual method of deriving the molecular weight of a gas from its density, merely by multiplying the latter by two (Chapter I., § 11), does not give strictly accurate results, since this procedure implies the truth of Avogadro's Hypothesis. If, however, the gas volume were to be measured at low pressures, the hypothesis would become more exact, and at zero pressure it would probably be quite exact. Of course, this is an impossible condition for measurement, but the density at zero pressure can be approximated to.

A clearer idea of the quantities to be measured may be gained by considering the subject in greater detail. Suppose a mass W gms. of gas occupies a volume v litres at 0° C. under a pressure of p atmospheres. The quotient W/pv is called the density per unit pressure. If the gas obeys Boyle's Law, pv is constant, and obviously the above quotient remains constant over the whole pressure range, but if the gas does not obey Boyle's Law, there is a continuous variation of W/pv as the pressure varies. If the limiting value of pv is taken as p approaches zero, and the value of pv is then p_0v_0, W/p_0v_0 is called the limiting density of the gas. This is the value to be used in determining molecular weights of gases.

If p_1v_1 is the value of pv when the pressure is one atmosphere, then obviously W/p_1v_1 is the normal density of the gas as commonly measured. Hence

$$\text{limiting density} = \text{normal density} \times (p_1v_1/p_0v_0).$$

It is thus a matter of some importance to determine the value of p_1v_1/p_0v_0, and this can be done by two distinct methods. The first is the extrapolation method. A number of determinations of pv are made for different pressures, and these are plotted and the curve extrapolated to zero pressure. This method is the one usually followed and is exemplified by the recent determinations of the atomic weights of nitrogen and phosphorus from the densities of their gaseous hydrides.

The second method depends on the assumption that the relative deviation from Boyle's Law is proportional to the pressure, and is obviously applicable only to those gases which do not greatly

deviate from Boyle's Law. The relative deviation is

$$\frac{p_0v_0 - pv}{pv}.$$

Hence, making the above assumption,

$$\frac{p_0v_0 - pv}{pv} = \alpha p.$$

α is known as the compressibility coefficient, and its value is obtained by taking two readings of pv between 0 and 1 atmosphere. In this case

$$p_0v_0 = p_1v_1(1 + \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

since $p_1 = 1$.

Thus, the limiting density = normal density/$(1 + \alpha)$.

Avogadro's Hypothesis can then be applied to the limiting density found by these methods.

It is clear that the expression (1) implies a linear relationship between p_0v_0 and p_1v_1. Whilst this is true in the majority of cases,

Pressure.	Density per Unit Pressure.
Atmos.	Gms. per litre.
1	0·77169
0·667	0·76773
0·5	0·76585
0·33	0·76383

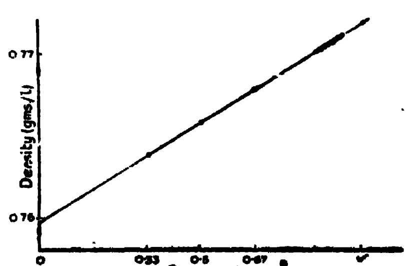


FIG. 59.—Graph of Pressure against Density per Unit Pressure for Ammonia.

there are some substances for which it is not true. For these a curved extrapolation must be used, and it was suggested by Guye that the result should be expressed in the form $p_0v_0 = p_1v_1\,(1 + \lambda)$. It has been pointed out by Cawood and Patterson (*J. C. S.*, 1933,

619) that λ has no physical significance like α, although it is frequently wrongly called the compressibility coefficient. It may perhaps be called the "effective compressibility coefficient."

As examples of the use of these equations the figures obtained by Moles and Batuecas in 1930 (*Anal. Fis. Quim.*, 1930, **28**, 871) for the density of ammonia, may be quoted.

These values are plotted in Fig. 59, and the curve continued to cut the density axis. The limiting density is found to be 0·75990 gm. per litre.

The limiting density of oxygen is 1·4277 gm. per litre, so the density of ammonia referred to oxygen as 16 is

$$\frac{0{\cdot}75990}{1{\cdot}4277} \times 16 = 8{\cdot}516.$$

The molecular weight of ammonia is therefore 17·032. Assuming the atomic weight of hydrogen to be 1·0078, this gives for the atomic weight of nitrogen 14·0086. The accepted value is 14·008.

Batuecas has also determined the density of nitrous oxide (*J. Chim. phys.*, 1931, **28**, 572). The following results were obtained :—

Pressure.	Density per Unit Pressure.
Atmos.	Gms./litre.
1	1·9804
0·667	1·9746
0·5	1·9722
0·25	1·9694

and

Pressure, p.	pv.
Atmos.	
1	1·00000
0·667	1·00294
0·5	1·00416
0·33	1·00559

By extrapolation of the curve between p and pv, the value for p_0v_0 was obtained, and $(1 + \lambda)$ came out to be 1·0085. The limiting density is therefore $\frac{1{\cdot}9804}{1{\cdot}0085} = 1{\cdot}9623$ gms. per litre.

The accepted figure for the volume occupied by one gram-molecule of a gas at N.T.P. is 22·414 litres.

Hence the molecular weight of nitrous oxide is $22{\cdot}414 \times 1{\cdot}9623 = 44{\cdot}014$, and the atomic weight of nitrogen is $\frac{1}{2}(44{\cdot}014 - 16) = \frac{1}{2}(28{\cdot}014) = 14{\cdot}007$.

The matter can be viewed in a somewhat different way. If Boyle's Law is true,

$$pv = RT,$$

where v is the volume occupied by one gram-molecule, R has its usual value (in litre-atmospheres) $p = 1$, and $T = 273°$ Abs.

If M is the molecular weight, and D the density in grams per litre,

$$M/v = D$$

But, $$v = RT/p.$$

Hence $$M = DRT/p.$$

This equation enables the molecular weight to be calculated if the density D is known at some temperature T, and pressure p, and holds, if Boyle's Law is true. This, however, is not the case. If we use Berthelot's equation (p. 208), it is obvious that

$$M = \frac{DRT}{p}\left(1 + \left\{\frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3}\right\}p\right),$$

which may be written

$$M = \frac{DRT}{p}(1 + Ap),$$

where A stands for the expression in brackets. From this relationship it is possible to calculate the molecular weight of a gas very accurately, if the critical data are known.

As an example we can calculate the molecular weight of nitrogen from the following data :—

Density at N.T.P. = 1·2507 gms. per litre.
Critical temperature = 125·96° Abs. $R = 0{\cdot}08204$ litre-atmos.
Critical pressure = 33·49 atmos.
Substituting in the equation

$$M = \frac{DRT}{p}\left(1 + \left\{\frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3}\right\}p\right)$$

we have

$$\begin{aligned} M &= 1{\cdot}2507 \times 0{\cdot}08204 \times 273\left(1 + \frac{9 \times 125{\cdot}96\,(273^2 - 6(125{\cdot}96)^2)}{128 \times 33{\cdot}49 \times 273^3}\right) \\ &= 1{\cdot}2507 \times 0{\cdot}08204 \times 273\,(1 - 0{\cdot}0002689) \\ &= 1{\cdot}2507 \times 0{\cdot}08204 \times 273 \times 0{\cdot}9997311 \\ &= 28{\cdot}01. \end{aligned}$$

Thus the molecular weight is 28·01.

If the density of a gas is known under two conditions of pressure and temperature, it is possible to calculate its true molecular weight, using the Berthelot equation, without knowing the critical temperature and pressure.

Thus, the density of neon at 0° C. and 0·5 atmos. is 0·44936 gm. per litre, whilst that at N.T.P. is 0·9002 gm. per litre.

In both cases

$$A = \frac{9T_c(T^2 - 6T_c^2)}{128p_cT^3},$$
$$= \frac{9\,T_cT^2}{128\,p_cT^3} - \frac{54\,T_c^3}{128\,p_cT^3}$$
$$= \frac{k}{T} - \frac{k'}{T^3},$$
$$= \frac{k}{273} - \frac{k'}{(273)^3}.$$

Since the temperatures are the same A will be the same, and the above process is not necessary; but where the temperatures are different it would have to be applied. Using the equation

$$M = \frac{DRT}{p}(1 + Ap),$$

for the first conditions

$$M = \frac{0{\cdot}44986\,R \times 273}{0{\cdot}5}(1 + A\,(0{\cdot}5)\,).$$

For the second conditions

$$M = 0{\cdot}9002\,R \times 273\,(1 + A)\;.\;.\;.\;.\;.\;(1)$$

$$\therefore\ 0{\cdot}44986 \times 2 \times 273\,R\left(1 + \frac{A}{2}\right) = 0{\cdot}9002\,R \times 273\,(1 + A).$$

or
$$0{\cdot}44986\left(1 + \frac{A}{2}\right) = 0{\cdot}4501\,(1 + A)$$
$$\therefore A = -\,0{\cdot}001066.$$

It is simplest to get M from equation (1);

$$M = 0{\cdot}9002 \times 0{\cdot}08204 \times 273 \times 0{\cdot}998934$$
$$= 20{\cdot}14.$$

(*b*) *Gay-Lussac's Law of Volumes.*—It has been found by experiment that Gay-Lussac's Law is not quite true. For example, Burt and Edgar found that the combining volumes of hydrogen and oxygen to form water were 2·00288 to 1. Gray and Burt found that two volumes of hydrogen chloride gave 1·0079 volumes of hydrogen. Guye and Pintza found that one volume of nitrogen

combined with 3·00172 of hydrogen to give ammonia. It is thus obvious that the law is not quite exact.

The deviations from the law exist because Avogadro's Law is not quite true, and this in turn depends upon the inaccuracy of Boyle's Law. At very low pressures, like Avogadro's Law, it would probably be true.

SUMMARY

THE behaviour of gases can be conveniently discussed by the application of the kinetic theory. This assumes that gases consist of molecules which are solid, spherical, and perfectly elastic. They move with random motion. Pressure is due to the bombardment of the walls of the containing vessel by the molecules of the gas. The average distance traversed by a particle between one collision and the next is the *mean free path*. The kinetic energy of a molecule depends only upon its temperature.

Using these assumptions, satisfactory derivations of Boyle's Law, Charles' Law, Avogadro's Hypothesis, Graham's Laws of Diffusion, and many other Laws governing the behaviour of gases, may be arrived at. The velocities of the molecules in different gases can be calculated. The root-mean-square velocity of hydrogen is 1838 metres per second at N.T.P.

The specific heat of a gas is different according to whether it is determined at constant pressure (C_p), or at constant volume (C_v). The ratio of the specific heats, $\gamma = C_p/C_v$, gives information concerning the atomicity of a gas. For monatomic gases, γ is about 1·67; for diatomic gases, 1·40; for triatomic gases, 1·33. γ may be determined (1) by direct determination of C_p (method of mixtures), and C_v (Joly's steam calorimeter); (2) by the method of Clément and Desormes; (3) by finding the velocity of sound in the gas, $v = \sqrt{\gamma p/d}$, where v is the velocity of sound in the gas, d the density, and p the pressure of the gas. The velocity of sound in the gas may be found directly, or indirectly, by comparing the wavelengths of the same note in two gases (Kundt's tube). A comparison of γ for the two gases may then be made.

The mean free path of the molecules of a gas may be calculated from observations of viscosity.

Avogadro's number, the number of molecules in one gram-molecule of a substance, may be found (1) by counting α-particles (Rutherford and Geiger). The number of atoms in a given volume of helium was counted. The α-rays shot off from radium consist of positively charged helium atoms. They can be counted by observing the scintillations produced by them when they impinge on a zinc sulphide screen. The volume of helium formed in a given time can be found by another experiment. (2) By observing the distribution of colloidal particles under gravity (Perrin). (3) By the Millikan oil-drop method. The results of these and other methods are remarkably concordant ($6·062 \times 10^{23}$).

In the mathematical derivation of Boyle's Law certain assumptions were made which were not justified. These lead to inaccuracies in the law, which is not obeyed by any gas. Numerous modifications of

Boyle's Law have been proposed, of which the most important are van der Waals' equation,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where a and b are constants, depending upon molecular attraction, and the volume occupied by the molecules, respectively, and Daniel Berthelot's equation,

$$pv = NRT\left[1 + \frac{9}{128}\frac{p}{p_c}\cdot\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

where p_c and T_c are the critical pressure, and critical temperature, respectively.

Avogadro's Hypothesis is also not quite accurate, and in careful determinations of molecular and atomic weights, deviations from it must be allowed for. This can be done by finding the limiting density (*i.e.*, the density per unit pressure corrected to zero pressure) by extrapolating the curve between pressure and density to zero pressure. It is assumed that, at zero pressure, Boyle's Law, and therefore Avogadro's Hypothesis, would hold. Accurate molecular weights may also be calculated by means of Berthelot's equation.

Deviations are also found in Charles' (or Gay-Lussac's) Law.

SUGGESTIONS FOR FURTHER READING

MEYER, O. E. "Kinetic Theory of Gases" (trans. R. E. BAYNES) (*Longmans*, 1899.)

LOEB, L. B. "Kinetic Theory of Gases." (*McGraw-Hill*, 1927.)

JEANS, J. H. "The Dynamical Theory of Gases." (*Cambridge University Press*, 1925.)

PERRIN, J. "Atoms" (trans. D. L. HAMMICK). (*Constable*, 1923.)

QUESTIONS

(1) What are the assumptions of the kinetic theory of gases, and how far are they justified? Show how Boyle's Law may be derived on the basis of this theory.

(2) What alterations in the other gas laws are necessitated in consequence of the fact that Boyle's Law does not hold with accuracy?

(3) What information concerning the atomicity of a gas can be obtained from a knowledge of its specific heats? Describe one method by which the ratio of the specific heats for a gas can be obtained.

(4) What do you understand by the terms "mean free path," "root-mean-square velocity"?

(5) Show how Graham's Law of Diffusion may be derived from kinetic considerations. Would you regard it as a true law, or are there deviations from it?

(6) Moles and Salazar (*Anales. Soc. Espan. Fis. Quim.*, 1932, **30**, 182) found the density of carbon monoxide under a pressure of one atmosphere and at 0° C., to be 1·25010 gms. per litre. The value for $(1 + \lambda)$ was 1·0050. The gram-molecule occupies a volume of 22·414 litres. Calculate the molecular weight of carbon monoxide and the atomic weight of carbon.

(7) Cawood and Patterson (*J. C. S.*, 1933, 619) give the following results for normal densities and " effective " compressibility coefficients :

Gas.	Normal Density.	$1 + \lambda$.
Ethylene	1·2606	1·0073
Carbon dioxide . . .	1·9767	1·0066
Nitrous oxide . . .	1·9777	1·0071
Sulphur dioxide . .	2·9265	1·0249
Dimethyl ether . . .	2·1100	1·0281

Calculate the molecular weights of these compounds, and the atomic weights of carbon, nitrogen and sulphur.

CHAPTER VI

LIQUIDS

SECTION 1.—LIQUEFACTION OF GASES

83. Critical Phenomena.—All gases can be liquefied if subjected to decrease in temperature and increase in pressure. The effect of temperature is rather more important than that of pressure, for whilst it is possible to liquefy all gases at atmospheric pressure, it is quite impossible to liquefy many of the known gases at atmospheric temperature. It was first found by Cagniard de la Tour, when experimenting with ether, that there is a temperature above which it is impossible to liquefy ether vapour, no matter what pressure is applied, but it was not until the work of Andrews on carbon dioxide that any significance was attached to this important observation. The temperature above which it is impossible to liquefy a gas, no matter what pressure is applied, is called the *critical temperature*. At this temperature, a certain pressure will have to be used to cause liquefaction, and this is called the *critical pressure*. The volume occupied by a certain mass of the gas at the critical temperature and pressure is called the *critical volume*, and is usually expressed as the volume in litres occupied by one gram-molecule of the gas at this temperature and pressure, though it is sometimes expressed as the ratio of the volume that the gas has at the critical temperature and pressure, to that which it would have at 0° C. and 760 mm. It is this value that is given in Table XXXVII. (p. 220).

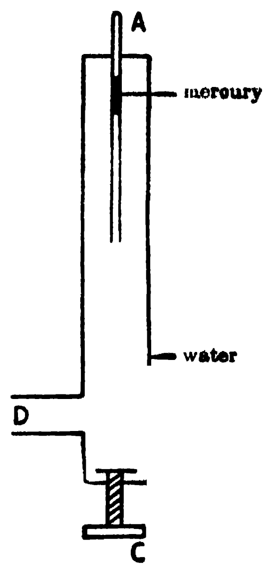


FIG. 60.—Andrews' Apparatus.

84. Andrews' Experiments with Carbon Dioxide.—In 1861 Andrews carried out his experiments on the effect of temperature and pressure on the volume of carbon dioxide. The

apparatus used consisted of a sort of hydraulic press, and is shown in Fig. 60. The tube A was a capillary tube, and contained the gas. It was closed by a mercury seal, held in position by capillary forces. This tube was placed in a copper vessel filled with water, and provided with a screw C at the bottom. An exactly similar tube with air in the capillary was joined at D, and served as a manometer. Pressure was applied to the gas by screwing up the screw C, and in this way a pressure of 400 atmospheres was obtained. The upper part of the carbon dioxide tube was surrounded by a heating bath, so that its temperature could be varied. It was found that above 31·1° C. no liquefaction would take place, no matter what pressure was applied to the gas.

The results of Andrews' experiments are given in graphical form

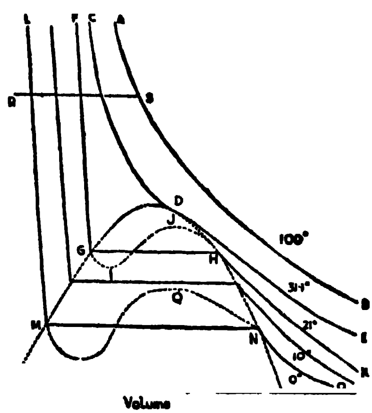


FIG. 61.—Isotherms for Carbon Dioxide.

in Fig. 61. The pressure is plotted against the volume, the curves thus obtained being called isotherms, as each curve applies, of course, to one particular temperature only. If the equation

$$pv = k$$

is plotted in this way, the curve obtained is a rectangular hyperbola, and this should be the curve obtained with a perfect gas. It is quite clear that carbon dioxide does not give a rectangular hyperbola, although, with increasing temperature, the curve approximates to one. The temperatures are marked on the various isotherms.

The isotherm AB shows the way in which p varies with v at 100° C. This is nearly a rectangular hyperbola, but deviates from the correct form slightly. The 31·1° C. isotherm has a marked deviation from the perfect form, and shows a slight bump at D. Below this temperature, the isotherms break up into three parts.

Consider the isotherm for 21° C., FGHK. The part KH represents the effect of pressure on the volume of the gas At H, liquid begins to appear, and the effect of the great volume change when this occurs makes itself apparent by the horizontal part of the curve, GH. When all the gas has liquefied, increase in pressure causes only a slight change in volume of the liquid, because liquids are so difficultly compressible. This is represented by the portion of the curve GF, which is almost vertical. It is sometimes possible to take the gas a part of the way over the dotted lines, HJIG, but this represents a metastable condition, and is difficult to realise. The isotherms below this temperature are all of the same form, as is shown by that for 0° C.

The isotherm, CDE, is the last one where liquefaction occurs, and therefore indicates the critical temperature and pressure. In this isotherm the horizontal portion has become reduced just to zero.

All gases have similar isotherms to those of carbon dioxide, although the critical temperatures vary greatly. It has been found that the ends of the horizontal portions of the isotherms, when joined, form a parabola, and the apex of this is, of course, on the critical isotherm.

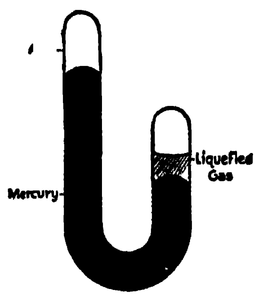


FIG. 62.—Determination of Critical Pressure.

85. The Determination of the Critical Constants.—The *critical temperature* is fairly easily found by sealing up some of the liquid gas in a strong glass tube and gradually warming it in a suitable bath. In the case of sulphur dioxide, or carbon dioxide, a gently heated water bath is suitable. The temperature at which the boundary between gas and liquid disappears is the critical temperature.

The *critical pressure* can be obtained by using the apparatus shown in the diagram. A quantity of the liquid and vapour is enclosed in one limb of the tube, and is separated from air in the other limb by a column of mercury. The limb containing the liquefied gas is gradually heated, as in the determination of critical temperature, until the boundary between liquid and gas disappears. The volume of the air in the opposite limb is then noted ; from this the critical pressure can be calculated.

The *critical volume* is rather more difficult to determine, but can be obtained from the rule of Cailletet and Mathias. The rule states that the mean values of densities of liquid and saturated vapour for any stable substance are a linear function of the temperature. Thus, if the density of a liquid is plotted against temperature, a curve

BC (Fig. 63) is obtained. If the density of the saturated vapour is plotted in a similar way, the curve AC is obtained. The two curves must meet at C, corresponding to the critical temperature; for, at this point, liquid and vapour become co-existent and identical, and the point C must give the critical density. It is the point at which the line CD intersects ACB, CD being the straight line obtained by joining the mean values of the density of the vapour and the liquid at a number of different temperatures, as stated by the rule of Cailletet and Mathias. The critical volume is readily obtained from critical density.

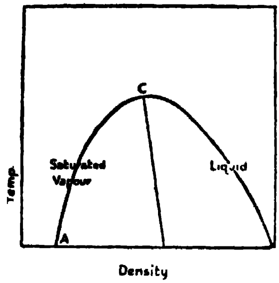


FIG. 63.

Some values of the critical constants for common gases are given in the accompanying table.

TABLE XXXVII.—CRITICAL CONSTANTS

Gas.	Critical Temp. °C.	Critical Press. Atm.	Critical Volume.
Hydrogen	− 234·5°	20	0·00264
Oxygen	− 118°	50	0·00426
Nitrogen	− 146°	33	0·00517
Carbon dioxide	31·1°	73	0·0066
Carbon monoxide	− 141·1°	35·9	0·00505
Air	− 140°	39	0·00468
Water	365°	194·6	0·00386

86. Continuity of State.—If the experiment on the determination of the critical temperature or pressure of a gas has been carried out, it will have been noticed that at the critical temperature the boundary of the liquid disappears. At this temperature, the liquid and the gas phases become identical. This is due to the reduction of the surface tension of the liquid to zero. The surface tension of a liquid decreases with temperature, so as the temperature of a liquefied gas is raised, the meniscus becomes flatter and flatter. Now, the surface tension measures the work that has to be done by the surface to increase its area. If the surface tension becomes very small, very little work will have to be done to increase its surface area. So, near the critical point, the surface becomes

unsteady, and ultimately disappears entirely, when the critical point is reached.

It is possible then to pass from gas to liquid, and *vice versâ*, without any abrupt change in state. Thus, take liquid carbon dioxide under conditions represented by the point R in Fig. 61. On heating this, we can suppose that its condition at any given temperature is represented by some point on the line RS, if its pressure is kept constant. Suppose it is heated to 100° C., then S will be on the 100° C. isotherm. Somewhere along the line RS the carbon dioxide will have become gaseous, though the change will not have been abrupt. The pressure may now be decreased, when the carbon dioxide, now gaseous, follows the isotherm AB. It is actually impossible to detect at what point the liquid becomes gas.

This phenomenon is termed "continuity of state."

87. Van der Waals' Equation, and the Critical Phenomena.— Remarkable confirmation of the general validity of van der Waals' equation is furnished by its application to critical phenomena. As already mentioned (p. 218), the isotherms obtained by plotting the curve

$$pv = k$$

are rectangular hyperbolæ. If we substitute van der Waals' equation for Boyle's Law, we have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Rearranging this in descending powers of v, we have

$$pv^3 - (RT + pb)v^2 + av - ab = 0$$

which is a cubic equation in v.

When plotted, the isotherms obtained are shown in Fig. 64, which gives the actual theoretical isotherms for carbon dioxide, calculated from equation (1). a has been taken as 0·00874, and b as 0·0023. By putting p and v equal to 1 and $T = 273$, a value for R is obtained. Then, substituting the values of p from about 40–120 atmos., corresponding values of v are deduced.

It is seen that the curves resemble the experimental isotherms of Fig. 61, with the horizontal part omitted; the latter is replaced by a curved portion, ABCD, resembling the dotted parts of the isotherms.

It has already been stated that these parts of the curve represent metastable conditions, *e.g.*, superheated liquid and supersaturated vapour. The whole course of the dotted lines, however, has never been realised experimentally.

It is possible, by choosing suitable values for p and T, to make

the cubic van der Waals' equation have equal roots. When this happens, the two humps AB and CD coincide, and a curve such as that shown at EF in Fig. 64 is produced. Comparing Fig. 64 with Fig. 61, it is seen that EF corresponds to the critical isotherm, CDE (Fig. 61). It should therefore be possible to calculate the critical constants by making use of the conditions that the equation should have equal roots.

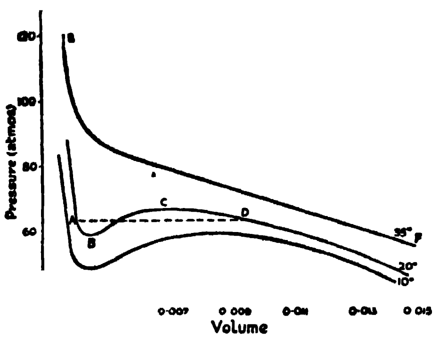


FIG. 64.—Theoretical Isotherms for CO_2.

When the three roots become identical, the root obtained, v, must be equal to the critical volume v_c.

$$\therefore v_c = v$$

and $$(v - v_c)^3 = 0.$$

Expanding this,

$$v^3 - 3v^2v_c + 3v_c^2v - v_c^3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Compare this with the expanded form of van der Waals' equation :—

$$pv^3 - (RT + pb)v^2 + av - ab = 0.$$

Bringing the coefficient of v^3 to unity,

$$v^3 - \left(\frac{RT + pb}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0 \quad . \quad . \quad . \quad . \quad (2)$$

When equation (2) has three equal roots, it must be identically equal to equation (1).

Equating the coefficients of v^2 in the two equations,

$$3v_c = \frac{RT + pb}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equating the coefficients of v,

$$3v_c^2 = \frac{a}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equating the numerical terms,

$$v_c^3 = \frac{ab}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From (4) and (5),

$$v_c = 3b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since when all the roots are equal the values of v, p and T in the equation are the critical values, v_c, p_c and T_c, the values of p and T obtained from equations (3), (4), (5) and (6) will be the critical values. Thus, from (5) and (6)

$$27b^3 = \frac{ab}{p},$$

$$\therefore p = p_c = \frac{a}{27b^2} \qquad (7)$$

Substituting (6) and (7) in (3), we have

$$\frac{RT + \frac{a}{27b}}{\frac{a}{27b^2}} = 9b \qquad (8)$$

$$\therefore T = T_c = \frac{8a}{27R} \qquad (9)$$

Summarising these results :—

$$v_c = 3b,$$

$$p_c = \frac{a}{27b^2},$$

$$T_c = \frac{8a}{27Rb}.$$

These results may be used to calculate the critical temperature of carbon dioxide.

Van der Waals obtained a, b, and R for carbon dioxide by substituting Regnault's values in his equation. In this way, a was found to be 0·00874,

$$b = 0{\cdot}0023$$
$$R = 1{\cdot}00646/273.$$

Hence $T_c = 8a/27Rb$

$$= \frac{8 \times 0{\cdot}00874 \times 273}{27 \times 1{\cdot}00646 \times 0{\cdot}0023}$$

$$= 305{\cdot}5^\circ \text{ Abs.}$$

The critical temperature is 305·5° Abs.

$$= 32{\cdot}5^\circ \text{ C.}$$

This is in comparatively good agreement with the observed value, 31·1° C.

88. The Theory of Corresponding States.—Instead of using the volume, pressure, and temperature of a gas in absolute units, the ratio of these quantities to the corresponding critical quantities could be used in van der Waals' equation.

Let $$\pi = \frac{p}{p_c} \quad ; \quad \varphi = \frac{v}{v_c} \quad ; \quad \theta = \frac{T}{T_c}.$$

The equation $$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

becomes $$\left(\pi p_c + \frac{a}{v_c^2\varphi^2}\right)(v_c\varphi - b) = RT_c\theta.$$

Substituting the values previously obtained for p_c, v_c, T_c, we have

$$\left(\pi \frac{a}{27b^2} + \frac{a}{9b^2\varphi^2}\right)(3b\varphi - b) = \frac{8aR}{27Rb}\theta$$

or $$\left(\pi a + \frac{3a}{\varphi^2}\right)(3b\varphi - b) = 8\theta ba$$

or $$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\theta.$$

φ is called the *reduced volume*, π the *reduced pressure*, and θ the *reduced temperature*. It is seen that this is a perfectly general equation holding for all gases, since the values of the critical constants have cancelled out. Hence this equation represents, as accurately as van der Waals' equation can, the isotherms of any gas. If two substances with the same reduced pressure and the same reduced temperature are taken, they will have the same reduced volume. The accuracy of this can be judged by considering the following table. When two or more substances have the same reduced pressure and temperature they are said to be in *corresponding states*. The law of corresponding states says that when this is so, the volumes of the substances will be the same fraction of their critical volumes.

In the table below, θ for each set is approximately constant, and it is found that φ (liquid) is approximately constant. The agreement is not so good for φ (vapour).

It has been found empirically that the boiling points of substances at atmospheric pressure are frequently about two-thirds of the critical temperature, both being measured on the absolute scale. This must not be regarded as perfectly general, but provides a certain amount of justification for comparing the properties of substances at their boiling points rather than at any other arbitrary

TABLE XXXVIII.—CORRESPONDING STATES [1]

$$\frac{p}{p_c} = \pi = 0{\cdot}08846.$$

Substance.	$\theta = \frac{T}{T_c}$	φ (Liquid).	φ (Saturated vapour).
Methyl alcohol . .	0·7734	0·3949	34·2
Ethyl alcohol . .	0·7794	0·4047	32·1
Propyl alcohol . .	0·7736	0·4028	31·1
Benzene . . .	0·7282	0·4065	28·3
Carbon tetrachloride .	0·7251	0·4072	27·4
Stannic chloride . .	0·7357	0·4021	28·1
Ether . . .	0·7380	0·4030	28·3

$$\varphi\ (\text{liquid}) = \frac{\text{vol. of liquid}}{\text{critical vol.}};\ \varphi\ (\text{satd. vap.}) = \frac{\text{vol. of satd. vapour}}{\text{critical vol.}}.$$

temperature, for the boiling points are, approximately, corresponding temperatures.

TABLE XXXIX.—BOILING POINT AND CRITICAL TEMPERATURE

Substance.	B. P. T_b. ° Abs.	Critical Temp. T_c ° Abs.	T_b/T_c.
Sulphur dioxide . .	263·0	430·25	0·611
Carbon dioxide . .	194·5	304	0·640
Chlorobenzene . .	405·0	633	0·641
Ether . . .	307·6	466·8	0·658
Benzene . . .	352·6	561	0·629
Water . . .	373·0	647·3	0·577
Ammonia . . .	234·5	404	0·580
Acetic acid . . .	391·5	594·6	0·658

In some cases the critical temperature of a substance is equal to the sum of its boiling and melting points on the absolute scale. The following table gives some examples of this. It will be noted that there are many deviations, and it must not be taken at all as a general rule.

[1] Data selected from values obtained by S. Young, 1892. For data for other substances see S. Young, "Stoichiometry" (Longmans, 1908), p. 219.

TABLE XL.—BOILING AND MELTING POINTS

Substance.	Melting Point. T_m.	Boiling Point. T_b.	$T_m + T_b$.	Critical Temp. T_c.
	° Abs.	° Abs.	° Abs.	° Abs.
Hydrogen	14	20·3	34·3	38·5
Oxygen	54	90	144	155
Nitrogen	62·5	77·3	139·8	127
Carbon dioxide	208	194·8	402·8	304
Ethylene	104	170·3	274·3	283
Ether	156	307·6	463·6	470

89. Liquefaction of Gases.—It is now possible to liquefy, and even solidify, all the known gases. The historical development of the liquefaction of gases will now be considered.

The first reference to an attempt to liquefy a gas was that of Boerhaave, who in 1732 tried to liquefy air. We now know that this attempt was particularly ambitious, for air resisted liquefaction for a long while. Boerhaave, like many another of the early workers, succeeded only in liquefying the water vapour in the air.

In 1799, Von Marum liquefied ammonia, one of the more easily liquefied gases, at ordinary temperatures by subjecting the gas to a pressure of about three atmospheres. In the same year, de Morveau, de Fourcroy and Vauquelin liquefied ammonia by using a freezing mixture which enabled them to reach the temperature of − 40° C., at this time a record in low temperatures. About this time, too, Monge and Clouet liquefied sulphur dioxide, another of the easily liquefied gases, merely by cooling. There is no doubt that erroneous conclusions were reached in much of this early work, owing to the very imperfect drying of the gases used, the condensation of the water vapour giving the impression that the gas itself had been liquefied.

In 1805, Northmore carried out some of the most important of the early work, and succeeded in liquefying chlorine, hydrogen chloride, and sulphur dioxide by applying pressure; but he failed with carbon dioxide, the apparatus exploding.

The work of Faraday carried out in 1823 is well known. He used a V-tube, in one limb of which the gas was prepared, whilst in the other it was liquefied under its own pressure, and with the help of external cooling. Faraday liquefied sulphur dioxide, hydrogen sulphide, carbon dioxide, nitric oxide, cyanogen and ammonia; and Davy, using the same method, liquefied hydrogen chloride.

Colladon tried to liquefy air by submitting it to high pressure and cooling. Air was confined in a thick glass tube, sealed with mercury, and so arranged that more mercury could be forced into the tube by hydraulic pressure. Although he reached a temperature of $-30°$ C., and a pressure of 400 atmospheres, the air was not liquefied. We now know that this was because the critical temperature had not been reached, and that no matter what pressure was applied above that temperature the gas would not liquefy.

Thilorier, using a Faraday's apparatus constructed of cast iron, tried to liquefy carbon dioxide, but the vessel burst. Later, however, he was able to liquefy, and even solidify, carbon dioxide, and was the first to use a freezing mixture of solid carbon dioxide and ether, giving a temperature of $-110°$ C., a temperature hitherto unreached.

In all the cases described above, a gas was liquefied by the action of pressure and cooling, either together or singly. Certain gases amongst which were hydrogen, oxygen, and nitrogen, were found to resist liquefaction under these circumstances, and they were therefore called the "permanent gases." They were not long to remain as permanent gases, however, for in 1877, Cailletet and Pictet succeeded in liquefying oxygen and hydrogen.

FIG. 65.—Faraday's Tube.

The various methods for liquefying gases that were used later, depend upon the development of methods for producing intense cold. These methods may be summed up as follows :—

(1) The use of freezing mixtures.
(2) Cooling by the adiabatic expansion of cold compressed gases.
(3) Cooling by the rapid evaporation of volatile liquids.
(4) Cooling by the Joule-Thomson effect.
(5) Cooling by adiabatic demagnetisation (de Haas).

(1) Freezing mixtures were used quite early in the history of the liquefaction of gases, as the above account shows. However, their use is very limited, for it is difficult to obtain a freezing mixture which gives a sufficiently low temperature.

(2) The method of cooling by the adiabatic expansion of a cold compressed gas was first made use of by Cailletet, who succeeded in liquefying air by this method. Air was expanded from high pressure, and the cooled air thus produced was used to cool incoming air. The effect was thus cumulative.

Cailletet had the idea for this method forced upon him more or less by accident, for he noticed that on reducing the pressure of some

gaseous acetylene, a thick mist was produced in the gas. Thinking this was only moisture he decided to try it with pure acetylene, and then discovered that the mist was actually made up of fine drops of the liquefied gas.

Cailletet constructed an apparatus with which he could liquefy many common gases. The gas was contained in a thick glass tube over mercury, and mercury was pumped in to compress the gas. The apparatus was so designed that the pressure could be quickly relieved, so that the gas could be alternately compressed and expanded with some rapidity. In this way he liquefied acetylene and nitrous oxide, and later carbon monoxide and oxygen, which had previously been regarded as "permanent gases."

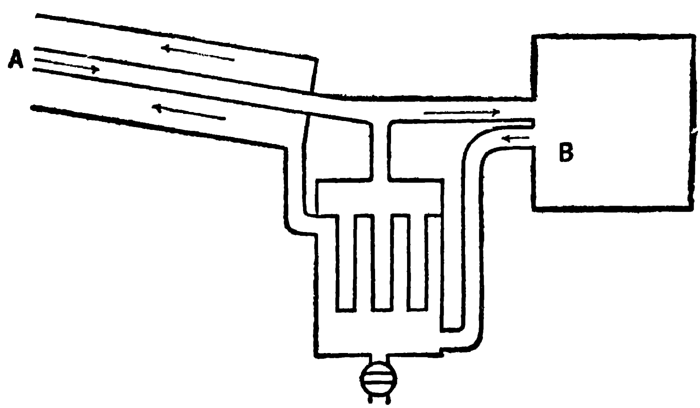


FIG. 66.—Claude's Apparatus.

Another application of this method was made by Claude, who liquefied air. This process enjoyed considerable popularity. The apparatus is represented diagrammatically in the figure.

The air was purified, and compressed to about 40 atmospheres and passed through the tube A into an apparatus B, in which it expanded, performing external work. The cooled and expanded air travels through the liquefier in the direction shown by the arrows, and finally passes along the outer tube of the heat exchanger A. In this way it cools the incoming gas, and this goes on until liquid air begins to collect in the liquefier.

(3) The fact that a liquid could be cooled by its own rapid evaporation was known as early as 1755, when water was frozen by rapidly evaporating it. In 1862 the first ammonia refrigerator was made. The method depends, of course, on the taking up of the latent heat of evaporation of the substance. This heat must be

supplied from somewhere, and it comes from the liquid. It was found possible by rapidly evaporating one liquefied gas to obtain a temperature low enough to liquefy another gas, and in this way the use of excessive pressures was avoided. Pictet was the first to use what is called the "cascade" method of liquefying gases. Pictet cooled a gas, B, below its critical temperature by the rapid evaporation of another gas, A, and then used the evaporation of the liquid, B, to cool another, C, and so on. In one series of experiments, sulphur dioxide was evaporated round carbon dioxide, which then liquefied fairly easily, and carbon dioxide was then allowed to evaporate round a tube of oxygen. On allowing the oxygen to expand a mist was formed which Pictet thought was solid oxygen, but which was probably the liquefied gas.

In 1883, Wroblewsky and Olschewsky cooled the condensing tube of Cailletet's apparatus with ethylene evaporating under reduced pressure, and further cooled by solid carbon dioxide. A little liquid oxygen was thus obtained.

It may be noted that the critical temperatures of hydrogen and helium (31° and 5·15° Abs. respectively) are so much below the temperatures attainable by the evaporation of gases of higher boiling point that the cascade method cannot be applied.

The lowest temperatures recorded before the work of de Haas on adiabatic demagnetisation were obtained by the use of liquid helium, boiling under reduced pressure. In this way, Kamerlingh Onnes reached a temperature of 0·82° Abs., and Keesom one of 0·71° Abs.

✓(4) When a highly compressed gas is allowed to expand into a region of low pressure so that no work is done against external pressure, a slight cooling effect is noticed. This is called the Joule-Thomson effect. The cooling is due to the fact that internal work is done by the gas in overcoming the attractive forces between the molecules, which have already been referred to in dealing with the van der Waals' *a* factor (§ 81). This effect is to be carefully differentiated from the cooling produced when a gas expands adiabatically, for in this case the gas does external work.

The Joule-Thomson effect would not exist if a gas were perfect, for then there would be no attractive forces between the molecules. It is greater the lower the temperature.

This effect is used in the Linde process for liquefying air. The apparatus is shown diagrammatically in Fig. 67. The air to be liquefied is first freed from impurities (carbon dioxide and water vapour), which would otherwise condense and block the apparatus. The air then enters the inner tube of the concentric pipes at A at a pressure of about 200 atmospheres. This tube is hundreds of yards

long, and is coiled spirally to save space. By regulating the valve C, the air is allowed suddenly to expand in the chamber D to a pressure of about 50 atmospheres. The air, thus chilled, passes back through the tube B which surrounds the tube A. The incoming air is thus cooled even more before it expands. The air that passes first through the apparatus goes back to the pumps, where it is compressed again to 200 atmospheres and passed through the apparatus again. Finally, liquid air issues from the jet. The tubes are all surrounded with insulating material, such as wool, feathers, etc.

Hydrogen behaves anomalously with regard to the Joule-Thomson effect. Instead of cooling when suddenly expanded, it warms up; and so it is clear that this method could not be applied to the liquefaction of this gas. When, however, the gas is cooled to about − 80° C., it behaves normally, and after this point, cools on expansion. This temperature is called the *inversion temperature.* Dewar liquefied hydrogen in 1898 by first cooling it to below the inversion temperature by means of liquid air, and then applying the ordinary Linde process.

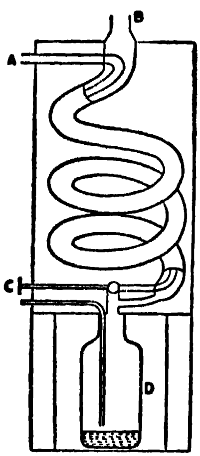


Fig. 67.—Liquefaction of Air (diagrammatic).

Helium also behaves like hydrogen, but has a much lower inversion temperature (− 240° C.) to which it can be reduced by cooling with liquid hydrogen. The Linde process is then applied, when the gas can be liquefied.

Helium has been solidified by Kamerlingh Onnes, who has carried out a great deal of research on the properties of substances at these very low temperatures.

Liquid air is manufactured in large quantities for the preparation of oxygen, though usually the process is continuous, the liquid air not being separated. For this purpose, the Claude method is employed for the liquefaction of air, and the apparatus for this is coupled to a Linde oxygen column.[1]

(5) Debye (1926) and Giauque (1927) came to the conclusion that when a magnetised body is demagnetised adiabatically (*i.e.*, in such a way that heat can neither enter nor leave the system), the temperature of the body must fall. This method has been tested practically by W. J. de Haas. It can be shown that the effect is best observed at low temperatures, and by substances which are not ferromagnetic. Using cerium fluoride, cooled before the demagneti-

[1] For details, see "Inorganic and Theoretical Chemistry," Sherwood Taylor (Heinemann), §678

sation process by liquid helium, de Haas was able to reach a temperature of 0·27° Abs.; later experiments, using dysprosium ethyl sulphate, gave a temperature of 0·14° Abs.; and, in July 1933, a temperature of 0·085° Abs. was attained, using cerium ethyl sulphate. de Haas believes that it will be possible by this method to reach the Absolute Zero.

The method is mentioned here merely as one of producing intense cold. It has not been, and is not likely to be, used for the liquefaction of gases.

90. Summary.—By cooling and compressing gases, they may be liquefied. There is, however, a certain temperature above which a gas cannot be liquefied, no matter how great is the applied pressure; this is the *critical temperature.* The pressure which must be applied at this temperature, to cause liquefaction, is called the *critical pressure.* The volume occupied by 1 gram-molecule of the gas at the critical temperature and pressure is the *critical volume.* The values of the critical temperature, pressure, and volume may be obtained in terms of the van der Waals' constants, a and b, by expressing the condition that the van der Waals' equation may have equal roots. The observed isotherms (pressure plotted against volume) of gases agree with the theoretical curve given by the van der Waals' equation. The ratios of the pressure, volume and temperature of a gas to the critical pressure, volume and temperature respectively are called the *reduced pressure, volume and temperature.* When two or more substances have the same reduced pressure and temperature, they will have the same reduced volume. (*Law of Corresponding States*).

Methods of liquefying gases depend upon the production of intense cold. This can be done (1) by the use of freezing mixtures, (2) by the adiabatic expansion of cold compressed gases, (3) by the rapid evaporation of volatile liquids, (4) by the use of the Joule-Thomson effect, (5) by adiabatic demagnetisation.

SECTION 2.—PROPERTIES OF LIQUIDS

A. Vapour Pressure

91. Definitions.—Every solid and every liquid possesses a vapour pressure which is a measure of the tendency of the substance to evaporate. Over every liquid there is a certain pressure of its vapour, the magnitude of which depends upon the temperature. Thus, if a liquid were to be sealed up in an evacuated tube, there would be molecules of the substance in the vapour state over the liquid, and they would exert a definite pressure. There is an equilibrium between the liquid and its vapour, as many molecules being lost from the surface of the liquid and then existing as vapour, as re-enter the liquid in a given time. The pressure of vapour

which exists over any liquid or solid at any temperature, the equilibrium condition having been attained, is called the *vapour pressure.*

The vapour pressure of a liquid varies a great deal with temperature, and if the values of the vapour pressure are plotted against temperature, a curve of the form shown in Fig. 68 is obtained.

When the vapour pressure of a liquid is equal to the pressure applied externally, the liquid boils, and evaporates freely.

It has been found, however, that the presence of any indifferent gas reduces the pressure of vapour in equilibrium with its liquid, although this is contrary to Dalton's Law of Partial Pressures. Hence, for accurate work, the *boiling point of a liquid is defined as the highest temperature that can be reached by a liquid under a given pressure of its own vapour when heat is applied externally and evaporation occurs freely from the surface.*

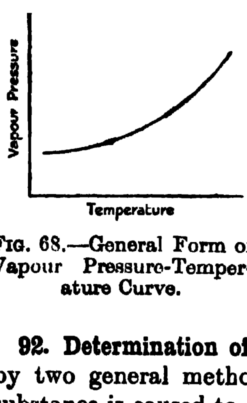


FIG. 68.—General Form of Vapour Pressure-Temperature Curve.

At 100° C., the vapour pressure of water is 760 mm., and hence water would boil at 100° C. when the pressure of water vapour over it is 760 mm. This will only differ a little from the temperature recorded when the total pressure is 760 mm.

When the vapour is in equilibrium with its liquid, it is said to be saturated vapour. When the pressure is less than this value, the vapour is said to be unsaturated.

92. Determination of Vapour Pressure.—This can be carried out by two general methods: (1) the static method, by which the substance is caused to evaporate in a Torricellian vacuum, and the depression of the mercury column is noted; and (2) the dynamic method, in which the liquid is made to boil under a definite pressure, and the temperature of the vapour is noted.

As an example of the first of these methods, two barometer tubes may be taken, filled with mercury, and inverted over mercury in order to form two barometers. One of these is kept for reference purposes, whilst about 1 c.c. of alcohol, or some other liquid is passed up the other by means of a bent pipette. After waiting a moment or two, the difference in height of the two barometers is measured, best by means of a cathetometer. This difference is due to the vapour pressure of the substance. There will also be a slight depression of the mercury due to the weight of the liquid added, but this may be neglected. The apparatus can be modified to give the vapour pressure at any given temperature by surrounding it with a heating jacket.

As a modern application of this method, the determination of the vapour pressure of carbonyl chloride below 18° C. may be quoted. Carbonyl chloride is a liquid which boils at 8° C. under atmospheric pressure. The apparatus used by the original workers (Atkinson, Heycock and Pope) is shown in Fig. 69.

The pure liquid was distilled directly into the flask, A, which was provided with a thermocouple, T, by means of which the temperature could be determined with accuracy. The flask was connected to a differential manometer by means of which the vapour pressure could be determined.

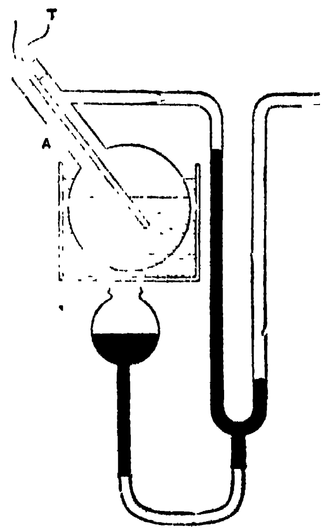


Fig. 69.—Apparatus for determining Vapour Pressure of Carbonyl Chloride below 18° C.

The method of Ramsay and Young gives results of a high degree of accuracy. The apparatus is shown in Fig. 70. A boiling tube, with fairly strong walls and provided with a side-tube, should be chosen for A. The rubber stopper closing this tube is provided with a tap-funnel, and a thermometer, the bulb of which is surrounded with cotton-wool tied on with thread. This should not be too thickly covered. The stem of the tap-funnel is bent so as just to touch the cotton-wool. The pressure gauge, B, consists of a long tube dipping into mercury. C is a large bottle—a Winchester bottle answers the purpose quite well—and serves to minimise the effect of leaks. D is a tube attached to a capillary, by means of which air can be slowly passed into the apparatus. The tube A is placed in a water-bath.

The first step is to test the apparatus to see that there are no leaks, and this is best done by evacuating by means of the filter-pump until a pressure of about 25 mm. is reached. When the pump is turned off, and the tap closed, there should be no alteration in this pressure after ten minutes. Having made sure that there are no leaks, a drop of the substance of which the vapour pressure is required is allowed to drop through the tap-funnel. The water-bath is now heated to about 50° C., as indicated by a thermometer (not shown in Fig. 70). The temperature indicated by the thermometer in A will be less than that of the bath, and after a little while it will become steady when the vapour pressure of the liquid is equal to

the pressure in the apparatus. Suppose that the temperature at the start is greater than this value. Then some of the liquid will evaporate and thus cool the thermometer. If the temperature is too low, some of the vapour will condense on the thermometer and warm it up. The steady temperature reached, and the height of the mercury in the pressure gauge, are read. When the latter reading is subtracted from atmospheric pressure, the vapour pressure of the liquid at the temperature of the thermometer in A is given.

By admitting air into the apparatus through D, further readings may be obtained at higher temperatures. For this, of course, the temperature of the heating bath will have to be raised a little.

Another method of determining the boiling point at different

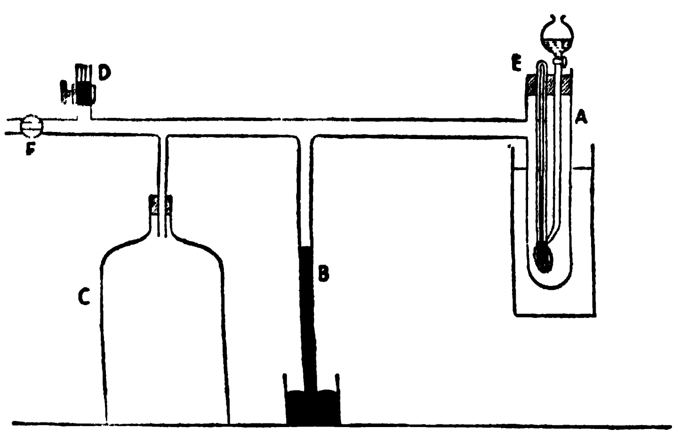


Fig. 70.—Ramsay and Young's Apparatus.

pressures, for that is all that has been done in the above experiment, has been devised by Smith and Menzies. The same apparatus for producing the reduced pressure is used (Fig. 70). A bulb-tube of the shape shown in Fig. 71 is blown, and is partly filled with the liquid under examination. It is attached to the thermometer by means of thread, and the tube is covered with high boiling paraffin placed in the boiling tube. The water-bath is heated to, say, 30° C. (it must be understood that this temperature will vary with the liquid used, and should be the lowest at which results of reasonable accuracy can be obtained), and the apparatus is evacuated. At first air bubbles, and later bubbles of vapour come from the bulb-tube, for the liquid is boiling under the reduced pressure. Now the pump is turned off by closing the tap F, and air is allowed to enter very slowly through D, until bubbles just cease to come from the tube

This means that the liquid is just on the point of boiling at the pressure and temperature indicated by the pressure gauge and thermometer respectively. The temperature of the heating bath is gradually raised, so that readings of the vapour pressure may be obtained at various temperatures. For accurate results, a correction should be applied because the bulb-tube is immersed to a certain depth in the oil, which should be measured. The density of the oil may be taken as 0·9.

Another method, that will be referred to again later in connection with the vapour pressure of solutions (§ 236), consists in passing a known volume of air over the surface of the liquid, and then determining the amount of vapour that has been removed, by weighing the liquid before and after the experiment.

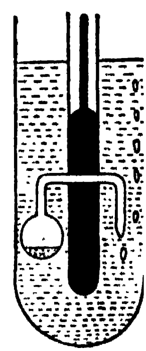


FIG. 71.—Smith and Menzies' Apparatus.

93. The Effect of Pressure on the Boiling Point of a Liquid.—It is obvious from what has been said that increase of external pressure will result in a rise in boiling point of a liquid. Thus, when specifying the boiling point of a liquid, it is, strictly speaking, necessary to mention the pressure. Thus, water boils at 100° C. only when it is in the presence of a pressure of its own vapour equal to 760 mm. of mercury. Below this pressure the boiling point will be lower; above it, it will be higher. Water can be superheated only when the pressure is increased.

The quantitative dependence of boiling point upon pressure can be obtained by the use of the Clapeyron-Clausius equation, which may be stated as

$$\frac{dP}{dT} = \frac{L}{T(v - v_1)}$$

where L is the molecular latent heat, v_1 and v are the volumes of 1 gm. mol. of liquid and vapour respectively at the boiling point T. This equation will be proved later (§ 319). It is thus seen that the rate of change of vapour pressure with temperature (dP/dT) is dependent upon the latent heat, and by a slight modification of the equation, the one may be calculated from the other.

The volume of the liquid which can be obtained by condensing a given volume of vapour is usually quite small, and can be neglected, so that the equation may be simplified to

$$\frac{dP}{dT} = \frac{L}{Tv}$$

If it can be assumed that the vapour obeys the gas laws (this is, of course, only an approximation), we have

$$Pv = RT$$

or

$$v = \frac{RT}{P} \quad \therefore \frac{dP}{dT} = \frac{LP}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From this equation we can calculate the latent heat if we know dP/dT, or the converse.

The best way of doing this is to proceed as follows. We know that

$$\frac{d \log_e P}{dT} = \frac{1}{P} \cdot \frac{dP}{dT}.$$

Hence, the above equation may be written

$$\frac{L}{RT^2} = \frac{d \log_e P}{dT},$$

from which

$$L = RT^2 \frac{d \log_e P}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If $\log_e P$ is plotted against T, the curve obtained is almost a straight line, of which the slope is $d \log_e P/dT$, and can easily be found. Substituting in the equation, L can then be obtained.

Another method which does not involve plotting can be used. If L does not vary much with temperature, we can integrate equation (1) above, obtaining

$$L = \left[R/\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] . \log_e \frac{P_1}{P_2} = R . \frac{T_1 T_2}{T_2 - T_1} . \log_e \frac{P_1}{P_2},$$

where P_1 and P_2 are the vapour pressures at T_1 and T_2 respectively. Substituting $R = 2$ gm.-cals., and converting to common logarithms, we have

$$L = 2 \times 2{\cdot}303 \frac{T_1 T_2}{T_2 - T_1} \log_{10} \frac{P_2}{P_1}$$

As an example, we may calculate the latent heat of evaporation of water over the range 90°–100° C. The following data are given: At 90° C. the vapour pressure of water is 526 mm.; at 100° C. it is 760 mm.

$$T_1 = 363° \qquad P_1 = 526$$
$$T_2 = 373° \qquad P_2 = 760$$

$$\therefore L = 2 \times 2{\cdot}303 \times \frac{363 \times 373}{10} \log_{10} \frac{760}{526}$$

$$= \frac{2 \times 2{\cdot}303 \times 363 \times 373 \times 0{\cdot}1598}{10}$$

$$= 10{,}200 \text{ gm.-cals. per gm. mol.}$$

The latent heat in gram-calories per gram is thus $\frac{10,200}{18}$

$$= 566 \cdot 5.$$

This is the average over the temperature range 90°–100° C. The experiment value for the latent heat at 100° C. is 539, and at 90° C. 549 gram-calories per gram.

94. Relationship between the Boiling Points of Related Substances. —By comparing the experimental values of the boiling points of various related liquids, Ramsay and Young discovered that there was a simple relationship between them. If the boiling points of the two substances under a pressure p_1 are T_1 and T_2, whilst those under a pressure p_2 are T'_1 and T'_2.

$$\frac{T_1}{T_2} = \frac{T'_1}{T'_2} = k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant.

It is to be noted that this relationship only holds between closely-

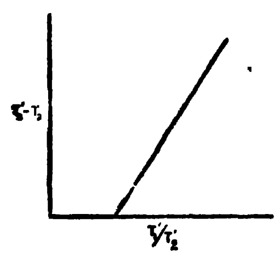


FIG. 72.—Graph of $(T'_2 - T_2)$ against T'_1/T'_2.

related substances, *e.g.*, benzene and toluene, chloro- and bromo-benzene, etc.

For substances not very closely related the relationship becomes

$$\frac{T'_1}{T'_2} = \frac{T_1}{T_2} + k\,(T'_2 - T_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k is usually very small, and is zero for very closely related substances, for then, obviously, equation (2) is identical with equation (1).

If T'_1/T'_2 is plotted against $(T'_2 - T_2)$, a straight line should be obtained, and this is usually the case.

Examples are known, however, of definite deviations from the straight line, and it is supposed that these are due to some abnormality in one or both of the liquids compared, such as association (*i.e.*, the existence in the liquid of molecular aggregates). Deviations are most frequently found in substances containing the hydroxyl group, and it is known that these compounds are usually associated.

95. Correction of Boiling Points to Normal Pressure—Crafts' Rule. —The boiling point of a substance is usually determined under the atmospheric pressure prevailing at the time of the experiment. This will be slightly different from that at 760 mm., and for purposes of reference and standardisation it is necessary that all boiling points should be corrected to 760 mm. This can be done by using a rule put forward by Crafts, based on the rule of Ramsay and Young, just discussed. The correction to be added to the boiling point observed, δT, is given by

$$\delta T = c\, T_0\,(760 - P)$$

where T_0 is the observed boiling point, P is the pressure at which it is measured, and c is a constant. The constant c has the value $\frac{1}{T} \cdot \frac{dT_0}{dP}$, where T is the normal boiling point.

For pure, normal liquids, the value of c is in the neighbourhood of 0·00012, but varies a little from substance to substance, and the value employed in any given case should be derived, if possible, from some closely related substance.

A few values of the constant, c, are given in the table below.

TABLE XLI.—CRAFTS' RULE

Substance.	c	Substance.	c
Benzene	0·000122	Methyl alcohol	0·000100
Toluene	0·000120	Ethyl alcohol	0·000094
Naphthalene	0·000119	Acetic acid	0·000107
Ethyl ether	0·000121	Water	0·000100
Ethyl acetate	0·000114	Chloroform	0·000119

B. MOLECULAR VOLUME

96. Definition.—*The molecular volume of any substance is the volume in cubic centimetres occupied by the molecular weight in grams.* It is obvious that it can be obtained by dividing the molecular weight of the substance by the density.

If Avogadro's Hypothesis were quite accurate, the molecular volumes of all gases would be the same, and equal to 22,414 c.c. Since it is not quite accurate, there are small deviations from this number for most gases.

It was owing to the application of Avogadro's Hypothesis to gases that the molecular volumes of solids and liquids were investi-

gated, in the hope that a similar generalisation might be made there. The success of this line of research was, however, very limited. With solids practically no useful results have been obtained, but with liquids there has been somewhat more success.

Dealing with the molecular volumes of solids, in a few cases this property has been found to be additive. Thus, if the molecular volumes of the halides of the alkali metals are compared, the substitution of one halogen for another is found to make the same difference in the molecular volume, and the substitution of one metal for another gives a characteristic difference in the molecular volume. This is clearly shown in the table below :—

TABLE XLII.—MOLECULAR VOLUMES OF ALKALI HALIDES

Salt.	Molr. Vol. c.c.	Pair.	Diffce.	Pair.	Diffce.
NaCl	27·1	KCl		NaBr	
KCl	37·5	— NaCl	10·4	— NaCl	6·7
		KBr		KBr	
NaBr	33·8	— NaBr	10·5	— KCl	6·8
KBr	44·3				
		KI		NaI	
NaI	43·5	— NaI	10·5	— NaCl	16·4
KI	54·0			KI	
				— KCl	16·5
				NaI	
				— NaBr	9·7
				KI	
				— KBr	9·7

An interesting point in this connection has to do with water of crystallisation. This may be attached to the anion of the salt or to the cation. In the two cases the molecular volume of the water is different. In the case of blue vitriol, it is well known that of the five molecules of water of crystallisation, four are more or less easily driven off, whilst one is held much more firmly, and it has been suggested that it might be called water of constitution. It is now known that the four molecules which are easily detached, are attached to the cation, whilst the other one is attached to the anion. Cationic water has a molecular volume of 14·6 c.c., the same as that calculated for ice at absolute zero. The molecular volume of anionic water is 10·0 c.c., which is the same as that found when

water combines with oxides to give acids, or bases. There is obviously a greater degree of combination in the second case.

97. Molecular Volumes of Liquids.—Kopp was the first to make an exhaustive study of molecular volumes. The first difficulty that confronted him was to decide at what temperature to measure the density. He took as his standard the boiling point of the liquid at atmospheric pressure. This was more or less an accident, but it was shown later to have been the right thing to do, for the boiling points are approximately the same fractions of the critical temperatures (§ 88). Other investigators have used other arbitrary temperatures, but whilst there are advantages associated with some, in general it may be said that the boiling point temperatures give the most regular results. Kopp's determinations were made by finding the density at ordinary temperatures, and then calculating that at the boiling point from observations of the coefficient of expansion. Since then, however, direct methods of determination have been devised.

As a result of his observations, Kopp propounded the law: "*the molecular volume of a liquid is equal to the sum of the atomic volumes of its constituent atoms.*"

This law is far from being exact. It is, however, approximately true. It has been found, and it is to be expected, that constitution plays a big part in deciding the molecular volume. It is to be

TABLE XLIII.—MOLECULAR VOLUMES OF ISOMERS

Substance.	Mol. Vol. c.c.	Diffce. %	Substance.	Mol. Vol. c.c.	Diffce. %
n-Hexane	140·0	2·5	Propyl aldehyde	75·4	2·4
Diisopropyl	136·5		Acetone	77·2	
n-Heptane	162·6	0·37	Ethylene chloride	85·3	4·0
Isoheptane	162·0		Ethylidene chloride	88·9	
n-Propyl alcohol	81·2	1·9	Aniline	106·4	4·6
Isopropyl alcohol	82·8		Picoline	111·5	
Methyl propyl ether	105·1	3·2	Ethyl benzoate	174·6	2·4
Butyl alcohol	101·9		Phenyl propionic acid	170·4	
n-Butyric acid	108·2	0·6	Diethylamine	109·0	2·6
Isobutyric acid	108·9		Butylamine	106·2	

expected that the atoms in a molecule will exert some influence on each other, and in some way distort the size of the atoms. That this is the case is easily seen from Table XLIII., giving the molecular volumes of isomeric compounds. Obviously, if Kopp's Law were correct, the molecular volumes of isomers should be the same, since they are made up of the same atoms. As the table shows, there are a number of differences, the largest being found where the isomers fall into two distinct classes, involving a complete change in constitution, *e.g.*, methyl propyl ether and butyl alcohol. This, however, is not always so. The dichlorethanes, for example, give large differences.

Besides giving the above law, Kopp made the following deductions :—

(1) Among analogous compounds, the same difference of molecular volume corresponds to the same difference in composition.

(2) By replacing two atoms of hydrogen by one atom of oxygen, the molecular volume is unchanged. This was later found to be untrue (see below).

(3) The atomic volume of carbon is twice that of hydrogen.

Kopp first found the molecular volume of the CH_2 group by considering a homologous series. Table XLIV. shows the mean

TABLE XLIV.[1]—VALUES FOR CH_2

Series.	No. of Intervals.	Maximum and Minimum.	Mean.
Alcohols	8	19·7–22·4	21·1
Fatty acids	8	21·6–23·4	22·4
Aldehydes (aliph.)	4	19·0–22·0	20·7
Amines (aliph.)	5	20·4–20·6	20·5
Alkyl iodides	10	21·1–24·3	22·6
Paraffins	13	—	22·7
Esters	15	21·2–27·7	24·4
Olefines	5	20·3–23·1	21·8

PARAFFINS

Paraffin.	Mol. Vol.	Difference.	Paraffin.	Mol. Vol.	Difference.
CH_4	38·5	—	C_5H_{12}	117·8	21·8
C_2H_6	56·7	18·2	C_6H_{14}	139·9	22·1
C_3H_8	74·6	17·9	C_7H_{16}	162·5	22·6
C_4H_{10}	96·0	21·4	C_8H_{18}	186·2	23·7

[1] The data for Tables XLIII. and XLIV. have been obtained from J. B. Cohen's "Organic Chemistry for Advanced Students," Vol. II. (Arnold).

values of the molecular volume of the CH_2 group obtained from many different homologous series. It will be noted that the value varies a good deal. Thus, in the series for the normal paraffins, shown in the second table, the value for CH_2 gets progressively greater as the series is ascended.

Kopp found the value 22 for CH_2. Using the third rule mentioned above, it follows that the amount due to C must be 11, and that due to H, 5·5. Then, from the second rule, O must be 11.

He soon found, however. that oxygen was a peculiar element to deal with. Its molecular volume varied with the states of its combination. Thus if the oxygen occurred in a carbonyl group it had a different value from that found when it occurred in the OH group or in an ether. The value for O in C=O is 12·2, whereas, for that in OH or in ethers, it is 7·8.

The table below shows the values that have been arrived at for the different elements.

TABLE XLV.—MOLECULAR VOLUMES OF THE ELEMENTS

C . .	11·0	Br .	27·8	O in OH or in ethers .	7·8
H . .	5·5	I .	37·5	O in >CO . .	12·2
Cl . .	22·8				

As an example, the molecular volume of acetone may be calculated. Assuming its structure to be $CH_3.C(=O).CH_3$, the molecular volume is given by 2 (27·5) + 11·0 + 12·2, ($2CH_3$ + CO) = 78·2.

Now, the molecular weight of acetone is 58, and its density at the boiling point is 0·78 gm. per c.c. The molecular volume observed is, therefore, $\frac{58}{0\cdot78} = 74\cdot35$.

98. Determination of Molecular Volume.—This involves determination of the density of a liquid at its boiling point. The old method used was to determine the density at 0° C., and then determine the coefficient of expansion of the liquid. From this, the density at the boiling point could be calculated. It is, however, quite easy to determine the density of a liquid at its boiling point directly.

The density of the substance, say ethyl acetate, is first determined at room temperature by means of a density bottle. A small bulb, of the shape shown in the figure, is weighed empty, and is then filled with ethyl acetate by warming and allowing to cool with the open end under ethyl acetate in a dish. The bulb filled with ethyl acetate is weighed. The difference in the two weighings gives the weight

of ethyl acetate taken, and since the density has been determined, the volume of the bulb can be calculated. The bulb is then suspended inside a flask containing ethyl acetate and provided with a reflux condenser. The ethyl acetate is boiled, and after a short time the liquid in the bulb reaches the boiling point. It expands, and a certain amount of the liquid flows out into the flask. When the liquid has been boiling for some minutes, the flask is allowed to cool, the liquid in the bulb contracts, and the bulb is taken out and weighed. The result gives the weight of ethyl acetate filling the bulb at the boiling point. The volume of the bulb is known, and hence the density at the boiling point can be calculated. The molecular volume is deduced by dividing the molecular weight of the substance by its density at the boiling point. The error in this method arises from the fact that no account has been taken of the expansion of the bulb when it is heated to the boiling point of the liquid. The actual volume occupied by the liquid at the boiling point is not the volume of the bulb at room temperature, but that at the boiling point, which will be a little greater.

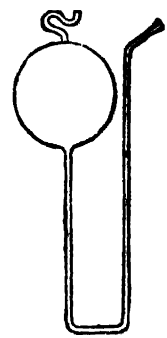


FIG. 73.—Tube for Molecular Volume Determination.

C. SURFACE TENSION

99. Definition.—Every liquid behaves as if it were enclosed by a skin or membrane. The surface of a liquid tends to contract, so that it must be under tension.

The *surface tension is defined as the force in dynes acting upon a line of* 1 *cm. length in the surface of the liquid.* Thus imagine that a cut of 1 cm. length is made in the surface membrane (the membrane, of course, does not exist, but the liquid behaves as if it does), there would be a force on each side of that line tending to open the slit, equal to the surface tension. Imagine a sheet of rubber stretched across the top of a beaker. The material is under tension. If a slit were to be made in the rubber, which was still kept under the same tension as before by some mechanical means, there would be a force on each side of the slit tending to open it.

The reason for the existence of surface tension has been mentioned when dealing with the critical phenomena (§ 81). The molecules of a liquid attract one another. A molecule in the bulk of a liquid is affected equally on all sides, but one at the boundary is only

affected on one side. It is therefore acted upon by a force which tends to drag it into the interior of the liquid. That is why liquid surfaces are characterised by the fact that they tend to become as small as possible. A drop assumes a spherical shape, because this is the form that has the smallest surface area for a given volume.

It is surface tension that produces the elevation of a liquid in a capillary tube, and this phenomenon can be made use of for the measurement of surface tension.

100. Determination of Surface Tension.—There are many methods which can be used for the determination of surface tension, all of which will be found described in text-books of physics. We shall describe here, briefly, two of them—the two which are most convenient, and are the most frequently used in the physical chemistry laboratory.

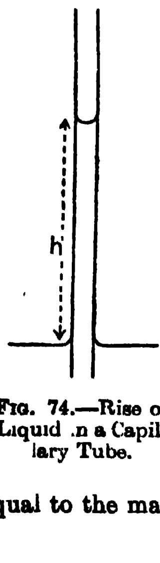


FIG. 74.—Rise of Liquid in a Capillary Tube.

(*a*) *The Capillary Rise Method.*—If a capillary tube is placed in a liquid it is found that the liquid usually rises in the tube. In one common case it falls, viz., mercury. Assuming that the liquid rises, suppose it reaches a height h above the level of the liquid outside. Suppose the density of the liquid is d, and the radius of the capillary tube is r. Then the force due to surface tension is $2\pi r\gamma$, since the periphery is $2\pi r$, and the surface tension γ. This must be equal to the mass of liquid raised, $\pi r^2 hdg$. Hence,

$$2\pi r\gamma = \pi r^2 hdg,$$

$$\gamma = \frac{rhdg}{2}.$$

This is only the very elementary theoretical treatment of the problem. For the corrections due to angle of contact, text-books of physics should be consulted.

To carry out the experiment, it is seen that it is necessary to determine the radius of the tube, and the height to which the liquid rises. The density of the liquid must be known, or must be found by another experiment. The radius of the capillary is best found by placing a thread of mercury 2 or 3 cm. long inside the tube and measuring its length at different points along the tube. If the length varies, another tube should be taken, for this indicates that the bore is not uniform. When the length has been measured accurately, the mercury is removed from the tube and weighed.

From the weight of the mercury, and its density, the latter being supposed known, the volume of the mercury can be obtained. The length occupied by the mercury in the tube is measured, so the area of cross-section and also the radius of the tube can be derived.

To determine the height to which the liquid rises in the tube, it is customary to use a cathetometer or travelling microscope.

From the results, the surface tension can be calculated, using the formula derived above.

(b) *The Drop-weight Method.*—The size of drop issuing from a capillary orifice is governed by the surface tension of the liquid. It was at first thought that the weight of a drop was proportional to the surface tension, but it is now known that the relationship is not so simple as this. Mathematical expressions have been derived for the relationship between the surface tension, radius of the tube, drop-weight, etc., from which the absolute value of the surface tension of a liquid can be obtained. The method is, however, more frequently used to compare surface tensions.

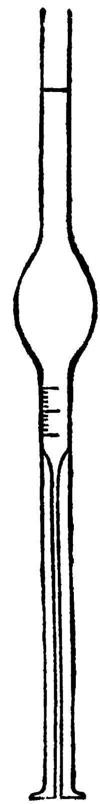


FIG. 75.—Stalagmometer.

The instrument employed is called a stalagmometer, and consists of a bulbed capillary tube, as shown in the figure. The tube is first cleaned out thoroughly with chromic acid mixture, and then with distilled water, and dried. It is then filled to the top mark with the liquid under observation. This is done by sucking up, as in a pipette. The tube is placed over a weighed weighing bottle, and 10 drops are allowed to fall into it. The rate at which the drops fall should be adjusted so that they come at about one every two seconds. If the liquid falls faster than this, the drops may not be properly formed, and may be too small. The weight of the 10 drops is found. The apparatus is then carefully cleaned out, and the experiment repeated with the other liquid. If m_1 and m_2 are the masses of 10 drops of the two liquids, and γ_1 and γ_2 are the surface tensions

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}.$$

If the surface tension of one liquid is known, that of the other is

readily calculated. Thus, if it is required to find the surface tension of benzene, the drop-weights of water and benzene would be compared, the surface tension of water being known, having been determined by some other method.

It is sometimes easier to determine the number of drops formed by a certain volume of liquid, instead of finding the mass of a drop. In this case the stalagmometer is filled to the top mark with the liquid under test, and the liquid is allowed to flow from the apparatus until the lower mark is reached, the number of drops being counted. The purpose of the small graduated portion of the tube is to enable fractions of a drop to be judged. The same procedure is adopted with the other liquid. Suppose that one liquid, of density d_1, produces n_1 drops, its surface tension being γ_1, and that the other liquid of density d_2, and surface tension γ_2, produces n_2 drops. Then

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} = \frac{vd_1n_2}{vd_2n_1}. \quad \therefore \frac{\gamma_1}{\gamma_2} = \frac{n_2d_1}{n_1d_2}.$$

The advantages of the drop-weight method are that it can be used at various temperatures by placing the whole apparatus in a thermostat, and that reliable results can be obtained rapidly. It suffers from the disadvantage that it is difficult to use for absolute determinations, and that the tip of the tube must be kept perfectly clean, otherwise bad results will be obtained. Care must be taken to avoid vibration during an experiment.

√ **101. Variation of Surface Tension with Temperature.**—The surface tensions of all substances vary with temperature. Usually there is a decrease as the temperature is increased. At first sight, over small temperature ranges, the relationship between surface tension and temperature appears to be linear, but when larger temperature ranges are used the graph of surface tension against temperature shows a curvature.

Van der Waals puts forward an equation expressing the relationship, which has been modified by Sugden to the form

$$\gamma = \gamma_0 (1 - T_r)^{\frac{6}{5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T_r is the reduced temperature (p. 224), and γ_0 is the surface tension of the supercooled liquid at absolute zero. γ is the surface tension at the reduced temperature T_r.

This equation is found to hold with some accuracy for most normal liquids, but there are deviations for liquids which are known to be associated, *e.g.*, the alcohols.

102. MacLeod's Equation.—There is a relationship between surface tension and density which has been found extremely useful,

as it forms the basis of the parachor (see next section). The equation was discovered by MacLeod in 1923, and states that

$$\gamma = C\,(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the surface tension, D is the density of the liquid, and d the density of the vapour, measured at the same temperature. The constant C is found to be independent of temperature, and the equation holds with accuracy over a large temperature range for normal liquids.

Reverting now to the effect of temperature on surface tension, Ramsay and Shields found that if the quantity $\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}}$, where M is the molecular weight, was plotted against temperature a straight line was obtained. What is the significance of $\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}}$? The molecular volume is $\left[\frac{M}{D}\right]$, and hence $\left[\frac{M}{D}\right]^{\frac{2}{3}}$ may represent the molecular surface. The surface tension measures the surface energy, and hence $\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}}$ is the molecular surface energy. The straight line referred to above does not pass through the origin, but the equation of the line is

$$\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}} = k\,(T_c - t - 6)$$

where T_c is the critical temperature, and t is the temperature of observation. This equation is referred to as the equation of Ramsay and Shields.

Some time previous to the derivation of this expression, Eotvos had put forward the equation $\gamma \left[\frac{M}{d}\right]^{\frac{2}{3}} = k\,(T_c - T)$, which is not so accurate as the Ramsay and Shields' equation.

This equation has been derived more recently by considering the effect of temperature on surface tension and on density. The equation of van der Waals and Sugden has already been mentioned (last section),

$$\gamma = \gamma_0\,(1 - T_r)^{\frac{6}{5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It has been shown by Sugden that if the surface tension, γ, is eliminated from MacLeod's equation and from the equation just given, an expression of the form

$$(D - d) = D_0\,(1 - T_r)^{\frac{3}{10}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is obtained connecting density and temperature. D_0 is the density of the supercooled liquid at the absolute zero.

It follows from (3) that

$$\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = \left(\frac{M}{D_0}\right)^{\frac{2}{3}} \cdot \frac{1}{(1-T_r)^{\frac{2}{3}}}.$$

Combining this with (2)

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = \frac{\gamma_0 M^{\frac{2}{3}}}{D_0^{\frac{2}{3}}}(1-T_r) = \frac{\gamma_0}{T_c}\left(\frac{M}{D_0}\right)^{\frac{2}{3}}(T_c - T),$$

i.e., $$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = k'(T_c - T).$$

This is Katayama's form of the Eotvos equation—$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = k(T_c - T)$—the forerunner of the Ramsay and Shields' equation.

Ramsay and Shields' equation is somewhat better than the Eotvos equation, but that of Katayama is better still, especially if $T_c - 6$ is substituted for T_c, making the equation

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = k'(T_c - T - 6).$$

It was at first thought that the value of the constant k or k' in these equations was the same for all normal liquids, and equal to 2·12. If any liquid gave a constant differing from this it was supposed to be abnormal. Many liquids, known from other experiments to be associated, such as the alcohols and water do give constants differing widely from 2·12, but it has since been shown that some perfectly normal liquids give anomalous values for k, so that this is no criterion of abnormality. (See association of liquids, p. 271.)

103. The Parachor.—It has been seen in dealing with molecular volume that the value of this property is, on the whole, additive, but that there are irregularities, even when the molecular volume is found at the boiling points, which are corresponding temperatures. The chief reason for this is the fact that every liquid has an internal pressure, due to the existence of attractive forces between the molecules. The internal pressures of various liquids are quite different, even at corresponding temperatures, and it is therefore to be expected that there will be anomalies in the molecular volumes. If we could correct for the varying internal pressure, we should obtain a property which would be truly additive.

To a certain extent, surface tension is a measure of internal pressure, for it is governed by the attractive forces between the molecules. The only reason why there is such a phenomenon as

surface tension is because there is an inward force acting on the molecules at the surface (§ 99). We look to surface tension, therefore, to throw some light on the correction to be applied to molecular volumes in order to make them free from anomalies.

For this purpose, Sugden made use of MacLeod's equation connecting surface tension and density,

$$\gamma = C\,(D - d)^4.$$

Another way of writing this equation is

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{D - d}.$$

Hence, for any liquid of molecular weight M,

$$\left(\frac{M}{D - d}\right) \gamma^{\frac{1}{4}} = MC^{\frac{1}{4}} = [P],$$

is constant. The constant $[P]$ is called the parachor. Since d is very small compared with D, the expression becomes the molecular volume multiplied by the fourth root of the surface tension. In other words, the *parachor is a measure of the molecular volume at temperatures at which different liquids have the same surface tension.*

The parachor is an additive property. There are definite values associated with each atom, and also with various structures, such as the double and triple bonds, the rings, etc. The table below gives some of the values in common use :—

TABLE XLVI.—PARACHORS

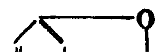
H	= 17·1	Triple bond	46·6
C	= 4·8	Double bond	23·2
O	= 20·0	3-Ring	16·7
N	= 12·5	4-Ring	11·6
S	= 48·2	5-Ring	8·5
Cl	= 54·3	6-Ring	6·1
Br	= 68·0	Single bond	0·0 (arbitrary)
I	= 91·0	Semipolar double bond	− 1·6
P	= 37·7	O_2 in esters	60·0

It is obvious that, since the parachor is a strictly additive property, it cannot be used to differentiate between isomers, unless these have certain structural differences.

104. Uses of the Parachor.—(1) *In deciding constitution.* In many cases the parachor has been of great use in deciding the

structure of a substance. For example, two structural formulæ have been proposed for quinone,

and



I II

To decide between these two, the value of the parachor may be determined.

To calculate the parachor for a substance of formula I, the values given in Table XLVI. are used.

6 Carbon atoms	$= 6 \times 4{\cdot}8$	$= 28{\cdot}8$
4 Hydrogen atoms	$= 4 \times 17{\cdot}1$	$= 68{\cdot}4$
2 Oxygen atoms	$= 2 \times 20{\cdot}0$	$= 40{\cdot}0$
4 Double bonds	$= 4 \times 23{\cdot}2$	$= 92{\cdot}8$
1 Six-membered ring		$= 6{\cdot}1$
		236·1

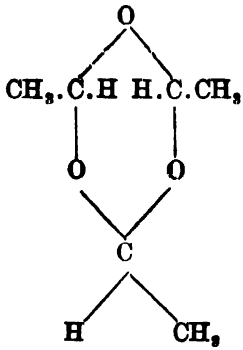
The parachor of the substance of formula II is obtained in a similar way :—

6 Carbon atoms	$= 6 \times 4{\cdot}8$	$= 28{\cdot}8$
4 Hydrogen atoms	$= 4 \times 17{\cdot}1$	$= 68{\cdot}4$
2 Oxygen atoms	$= 2 \times 20{\cdot}0$	$= 40{\cdot}0$
3 Double bonds	$= 3 \times 23{\cdot}2$	$= 69{\cdot}6$
2 Six-membered rings	$= 2 \times 6{\cdot}1$	$= 12{\cdot}2$
		219·0

The value found by experiment is 236·8, indicating that, without doubt, the first is the correct formula.

Acetaldehyde condenses to form paraldehyde, which is made up of three molecules of acetaldehyde. The parachor of paraldehyde, however, is 298·7, which is much less than three times the parachor of acetaldehyde ($121{\cdot}2 \times 3 = 363{\cdot}6$). The atoms must therefore be arranged in a somewhat different manner in paraldehyde from acetaldehyde. A cyclic formula for the substance (I) has been suggested, and this gives a parachor of 300·1, whereas the straight

chain formula (II) gives a parachor of 317·2. It is clear then that paraldehyde possesses a ring structure.

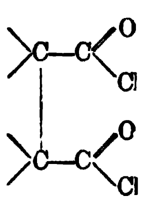


I

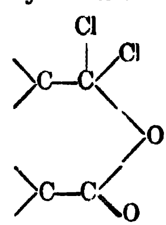
$CH_3.CH(OH).CH_2.CH(OH).CH_2.CHO$

II

Another example of the use of the parachor in deciding structural problems, is the application to the determination of the constitution of the chlorides of certain dibasic organic acids. The formula usually assigned to these compounds is I (below). Sometimes, however, they appear to behave as if they had the constitution II (below). Succinyl chloride, for example, has been regarded as a mixture of the two forms, though more recent chemical evidence leads to the conclusion that it is best represented by the symmetrical formula I.



I



II

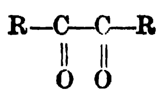
Phthalyl chloride exists in two isomeric forms, one having the melting point 15°, the other 88·5°. It has been stated by Ott and Pfeiffer that the lower melting form is the more stable, and has a

Substance	[P] obs	[P] calc	
		Formula I	Formula II
Succinyl chloride . . .	282·6	282·6	267·9
Phthalyl chloride (m.p. 15°) .	373·9	377·5	362·8
Phthalyl chloride (m.p. 88·5°) .	367·8	377·5	362·8

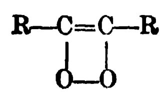
symmetrical formula, whilst the higher melting point modification has the unsymmetrical formula. The evidence provided by the parachor as to the structure of these compounds is summarised in the table on p. 251.

It is clear that succinyl chloride possesses the symmetrical formula. With phthalyl chloride the parachors do not agree with the theoretical for either form, though it is clear that the parachor of the higher melting form is less than that of the lower melting one. This would indicate that the higher melting form was the one with the unsymmetrical formula. Actually, there was a progressive change in the nature of the substance during the determination of the surface tension, so that the deviations from the theoretical values are easily explained. It is seen, then, that in this case the parachor supports the chemical view.

The structure of benzil and its derivatives has also been investigated by this method. They have been variously regarded as diketones or as peroxides (I and II respectively).



I



II

The parachor of benzil is 480·8, whereas that calculated from formula I is 476·0, and that from formula II is 464·4. Benzil, therefore, possesses the diketone formula.

Many other structural problems have been elucidated by means of the parachor, for details of which the reader should consult Sugden's "*The Parachor and Valency.*"

(2) The concept of the parachor has been of use in questions of *valency*, and particularly because it indicates the existence of two kinds of double bond. If we draw up a table showing the parachors for a series of compounds containing double bonds, we find that in some cases the parachor for the double bond has a positive value about 23, whilst in others it has a negative value of about − 1·6.

According to the electronic theory of valency there are two types of bond—one electrovalent, the other covalent. In the first instance, electrons are completely transferred from the orbit of one atom to that of the other, whilst in the second, the electrons are shared (see Chapter IV.). A double bond can therefore be made up of (*a*) two covalencies, (*b*) two electrovalencies, (*c*) an arrangement analogous to one covalency and one electrovalency. In the first case, the parachor has a positive value of about 23; in the second, no positive information of what would happen is available, for most of the substances having this type of linkage are inorganic

solids, and so far no experiments have been devised to cope with them; in the third case we have the negative parachor, − 1·6. This third type of linkage is called the co-ordinate linkage, or the semipolar double bond, and exists in substances like thionyl chloride, $Cl_2S \rightleftharpoons O$.

TABLE XLVII.—PARACHORS OF SUBSTANCES CONTAINING DOUBLE BONDS

		[P] obs.	[P] calc.[1]	Difference.
Containing covalent linkages.	Ethylene $CH_2 = CH_2$	99·5	78·0	21·5
	Acetone $(CH_3)_2C = O$	161·5	137·0	24·5
	Carbon disulphide $C(=S)_2$	144·7	101·2	21·8 × 2
	Nitrosyl chloride $Cl.N{=}O$	108·1	86·8	21·3
Containing co-ordinate linkages.	Phosphorus oxychloride $Cl_3P \rightarrow O$	217·6	220·6	− 3·0
	Thionyl chloride $Cl_2S \rightarrow O$	174·5	176·8	− 2·3
	Dimethyl sulphate $(CH_3O)_2S(\rightarrow O)_2$	238·9	240·4	−0·75 × 2
	Sulphuryl chloride $Cl_2S(\rightarrow O)_2$	193·3	196·8	−1·65 × 2

[1] The sum of the parachors omitting the double bond.

105. Molecular Volumes at Absolute Zero.—The MacLeod equation (§ 102),

$$\gamma = C\,(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

connects the surface tension γ with the density D of the liquid, and that, d, of the saturated vapour.

Van der Waals proposed an equation connecting surface tension and temperature (§ 101).

$$\gamma = \gamma_o\,(1 - T_r)^{\frac{5}{4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

T_r is the reduced temperature, and γ_o the surface tension of the supercooled liquid at absolute zero.

Combining (1) and (2), we have

$$\gamma_0 (1 - T_r)^{\frac{6}{5}} = C (D - d)^4,$$

or

$$(D - d) = c_1 (1 - T_r)^{\frac{3}{10}}.$$

When the supercooled liquid at absolute zero is considered,

$$T_r = 0, \text{ and } c_1 = (D_0 - d_0) = D_0 \text{ (approx.)},$$

where D_0 is the density of the supercooled liquid at absolute zero, and d_0 is that of the saturated vapour at that temperature. It is thus possible to obtain the density of a liquid at absolute zero, and by dividing this into the molecular weight, the molecular volume V_0 at the absolute zero is derived. This quantity is also called the zero volume.

Zero volumes have been calculated in this way by Sugden (1927), and a series of atomic and structural constants has been drawn up. Biltz (1926–27) has also derived a series of zero volumes by quite other methods, including extrapolation of liquid densities, densities in the solid state, and limiting molecular volumes obtained from the X-ray analysis of crystals. Unlike Sugden, who supposed that the zero volume was a simple additive relationship, Biltz finds that the relationship is of the form $V_0 = \Sigma\ (nv_0/m)$, where V_0 is the zero volume of the compound, v_0 the zero volume of any one constituent free element, and n/m a coefficient. The last is frequently unity, but for hydrogen it is equal to 0·5. Although the methods used by Biltz were entirely different from that of Sugden, the structural and atomic constants derived by both investigators agree fairly well.

It is clear that it ought to be possible to calculate the distances between the molecules in a compound at absolute zero from the observations of zero volumes. This has been done by Sugden (1929). The results obtained bear a constant ratio to those derived by other methods (viscosity and the parachor respectively); this ratio can be adequately explained. It is considered that the parachor, comparing as it does the molecular volumes at equal surface tensions, largely eliminates the effects of the intermolecular fields, and so gives different results for the molecular diameters from those obtained from zero volumes.

Zero volumes are probably not strictly additive, as some molecules will have peculiar intermolecular fields. When the effect of the latter is eliminated, a truly additive function would be expected, and indeed is found in the parachor.

D. Viscosity

106. Definition.—All liquids possess a certain resistance to flow, which is called their viscosity. It is really a frictional effect due to

the passage of one layer of liquid over another, and is sometimes referred to as such.

The *coefficient of viscosity* is defined as *the force required per unit area to maintain unit difference of velocity between two parallel planes in the fluid, one centimetre apart.*

The smaller the coefficient of viscosity, the more rapidly does the liquid flow. The greater it is, the less rapidly does the liquid flow. Oils, and liquids like glycerine, have a very high coefficient of viscosity, whilst ether and liquids which we are accustomed to call "very mobile," possess a low coefficient.

The coefficient of viscosity is expressed in dynes per sq. cm. The unit of viscosity is called the poise (from the name of the investigator who did most of the early work in the subject—Poiseuille).

107.—Determination of Viscosity.—It can easily be shown that

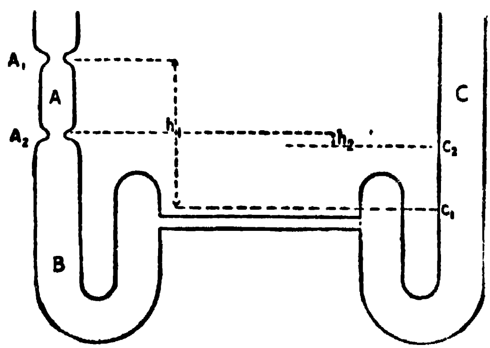


FIG. 76.—Diagram of Koch's Apparatus (after J. Newton Friend).

when a liquid flows through a capillary tube of radius r, for a time t, under a constant pressure head p, the volume of liquid v, issuing from the tube, is given by

$$v = \frac{\pi p t r^4}{8 l \eta} \qquad (1)$$

where η is the coefficient of viscosity and l is the length of the tube.

For the purposes of a simple experiment, it is possible to keep the pressure head almost constant by having a large reservoir of water and by carrying out the experiment over not too long a time. The fall in level of the liquid in the reservoir will then not be appreciable. For this experiment, a capillary tube of known length is connected to the bottom outlet of an aspirator, and at a given instant a tap is opened and the liquid is allowed to flow through the tube. After the flow has continued for a definite time, determined by means of a

stop-watch, the tap is closed, and the volume of liquid that has come through is measured. The radius of the tube is determined by measuring the length and mass of a mercury pellet placed in the tube. The tube should, of course, be selected for uniformity of bore, and the temperature must be kept quite constant throughout the experiment.

For the accurate determination of the coefficient of viscosity, it is necessary to take into account the fact that the pressure head is not constant, and this can be done by an extension of the formula given above.

The apparatus used for a more accurate determination is that due to Koch, and shown in outline in Fig. 76.

The tubes A, B and C, have the same radius, r_1, the liquid in A being allowed to fall from the mark A_1 to A_2. During this time the liquid rises in C from C_1 to C_2. In the diagram, h_1 and h_2 will be the initial and final pressure heads. Suppose the time taken for the liquid to fall from A_1 to A_2 is t secs.

In a small time dt secs., a volume dv of liquid will have passed through the capillary tube. If the pressure head at this moment is h,

$$dv = \frac{\pi h g d r^4}{8l\eta}\, dt,$$

where r is the radius of the capillary and d the density of the liquid. But, in the experiment

$$dv = -\pi r_1^2 \frac{dh}{2}, \quad \therefore \quad v =$$

If we substitute this value for dv in the above equation we have :—

$$-\frac{\pi r_1^2}{2}\, dh = \frac{\pi h g d r^4}{8l\eta}\, dt.$$

Integrating,
$$\frac{-\pi r_1^2}{2}\left[\log_e h\right]_{h}^{h_2} = \frac{\pi g d r^4}{8l\eta}\left[t\right]_0^t,$$

$$\therefore \quad \frac{r_1^2}{2}\log_e\frac{h_1}{h_2} = \frac{gdr^4 t}{8l\eta},$$

$$\eta = \frac{2gdr^4 t}{8lr_1^2 \log_e \frac{h_1}{h_2}}.$$

but
$$v = \pi r_1^2\,\frac{h_1 - h_2}{2},$$

$$\therefore \quad \eta = \frac{\pi(h_1 - h_2)\, gdr^4 t}{8lv \log_e \frac{h_1}{h_2}}.$$

As already stated, it is a difficult matter to determine the absolute coefficient of viscosity for a liquid, and, indeed, it is not usually necessary. As with surface tension, the relative viscosity of a liquid with respect, say, to water, may be determined; and then, knowing the coefficient of viscosity of water, which has been found by another experiment, the coefficient for the other liquid may readily be found.

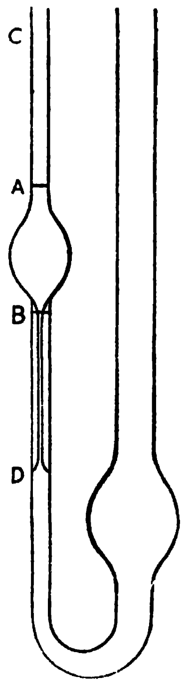


FIG. 77. — The Ostwald Viscometer

ay to do this is to make use of the Ostwald viscometer. This consists of a tube of the form shown in Fig. 77. The wider limb of the tube is first filled with the liquid under examination, say water, and it is then sucked up to a level C in the narrow limb. The water is then allowed to flow back, and the time taken for the level to fall from A to B is noted. The liquid passes through the capillary tube BD, and it is clear that the time of flow, t, will be proportional to the coefficient of viscosity. This follows from equation (1) (p. 256). It is also inversely proportional to the density d, from this equation. Hence,

$$\eta = kdt.$$

For a second liquid

$$\eta' = kd't'$$

Hence
$$\frac{\eta}{\eta'} = \frac{dt}{d't'}$$

If the coefficient of viscosity of water is known, the coefficient for the other liquid is readily found.

The result will not be quite accurate, since the pressure head will not be quite the same for the two liquids, owing to their differing densities.

With this apparatus it is quite easy to compare viscosities at different temperatures. The whole apparatus may be placed in a thermostat. Of course, it is necessary to maintain the temperature constant during an experiment.

There are many other types of viscometer depending upon such phenomena as the fall of a sphere through a liquid, or the force required to twist one plate relative to another in a liquid, but there is no need to describe them in detail here.

108. Viscosity and Constitution.—The relationships between viscosity and constitution are not very marked, though a few points

have been noted. For example, in homologous series, the increase in viscosity per CH_2 group is roughly constant.

A useful relationship between viscosity and molecular volume was discovered by Dunstan; it may be expressed as follows:

$$\frac{d}{M} \cdot \eta \times 10^6 = 40 \text{ to } 60,$$

where d is the density, M the molecular weight and η the coefficient of viscosity of the liquid. This relationship holds only for normal liquids. For associated liquids, the number is considerably greater than this. The values for a few substances are given in the table below :—

TABLE XLVIII

Substance		Formula	$\frac{d}{M} \cdot \eta \times 10^6$
Normal Liquids.	Benzene	C_6H_6	73
	Toluene	$C_6H_5.CH_3$	56
	Acetone	$CH_3.CO.CH_3$	43
Abnormal Liquids.	Water	$H.OH$	559
	Glycol	$CH_2OH.CH_2OH$	2,750
	Glycerol	$CH_2.OH.CHOH.CH_2OH$	116,400

This expression has been used as a criterion of association (p. 272).

Thorpe and Rodger introduced the term molecular viscosity; it is an additive property at the boiling point. We have already met the term molecular surface when dealing with surface tension. If the molecular surface is multiplied by the coefficient of viscosity, the molecular viscosity is obtained. Translated into ordinary language, this means the force in dynes which is required to maintain a molecular surface in motion at a velocity of 1 cm. per sec., relative to another molecular surface at a distance of 1 cm. from it. The following structural and atomic constants were arrived at :—

H	80	S	155
C	−98	Cl	284
O (in OH)	196	Double bond	113
O (in ethers)	35	Iso-union	15
O (in >C = O)	248	Ring formation	610

It has also been found that the logarithm of the coefficient of viscosity is an additive property. The following values have been obtained for the various atomic and structural constants :—

	$\log \eta \times 10^6$		$\log \eta \times 10^6$
CH_2 . .	+ 0·107	$COOC_2H_5$ . .	+ 1·573
H . .	+ 0·934	C	− 1·761
OH . .	+ 2·102	Double bond .	+ 1·847
CO . .	+ 0·407	Iso-union . .	− 0·030
O (in ethers)	+ 0·098		

Let us test this with ether. The coefficient of viscosity of ether at 20° C. is 0·00237.

	$\log \eta \times 10^6$
$4CH_2$	0·428
2H	1·868
O (ethereal). . .	0·098
	2·394

Antilog 2·394 = 247·7.

Hence viscosity should be 0·002477, in good agreement with the experimental value.

It must be stated, however, that these relationships have not proved of any value in the solution of structural problems.

E. Optical Properties

(a) Optical Activity

109. Polarisation of Light.—By the term "optical activity" is understood the power possessed by certain substances to rotate the plane of polarisation of light.

Ordinary light may be supposed, for our present purpose, to be a transverse wave-motion. The oscillations which make up a train of waves are at right angles to the direction of propagation, but may take place in any plane. Thus if a ray of light were travelling in the plane of this paper, the transverse oscillations themselves might take place in any plane, in the paper, or out of it. Some might be at right angles to the plane of the paper, others at 45°, or any other angle. All that is meant by saying that light travels in a certain direction is that the direction of travel of the waves is the same. No direction is specified for the actual oscillations.

If, by any means, light can be obtained in which the oscillations are all in one plane, the light is said to be polarised. Thus, if we have light travelling in the plane of this paper, and by some means or other we make all the oscillations of the light take place in the plane of the paper too, then we have light which is polarised in the plane of the paper. This plane polarisation may be brought about by various means. Thus, when light is reflected from certain

surfaces there is always a considerable degree of polarisation. It may be noted here that it may not be possible to polarise a beam of light completely, but it may be possible to get the greater proportion of oscillations to take place in one plane. When light passes through certain crystals in a certain direction, it may emerge polarised. One of the best crystals for this purpose is calcite, which has the property of double refraction. When light falls on to a calcite crystal, it is split up by the crystal into two rays, the crystal appearing to possess different refractive indices for the two rays. The first is called the ordinary ray, the second, the extraordinary ray. Now, on examination, both these rays are found to be polarised, one in a plane at right angles to the other. If a crystal of calcite is so cut that only one of the rays emerges, the other being returned by internal reflection, a beam of polarised light is produced. A calcite crystal cut in this manner is called a Nicol prism.

If the beam of light emerging from a Nicol prism is passed on to another similar prism, it will get through if the second prism is in exactly the same position as the first, but if turned so that it is at 90° to the first, no light will get through, but it will all be totally internally reflected.

An illustration from Stewart's "Stereochemistry" will make this quite clear. Suppose we have two books lying on a table. A flat ruler may be made to pass through both of them. If, however, one book is placed so that its plane is at right angles to that of the other, the ruler which gets through one will not be able to get through the other. The first book stands for the first Nicol prism. Light emerging from it will be polarised in one plane—this is represented by the ruler. If this polarised light falls on another Nicol prism it may get through or it may not, it depends upon the relationship of the second prism to the first. If its crystal planes are in the same planes as those of the first the light will get through, just as when the leaves of the second book are in the same planes as those of the first, the ruler gets through. If they are at right angles then no light gets through. The illustration fails, of course, in that a slight variation of angle between the two books means the cutting off of all possibility of the ruler from getting through, whereas in the case of light, total darkness is only attained when the two crystals are exactly at right angles to each other.

Now, certain liquids and solids are capable of rotating the plane of polarisation of light. If such a liquid is interposed between two parallel Nicols, it is found that the one no longer has to be turned through a complete right angle to get total darkness, but that they have to be at some other angle to each other. This is because, during its passage through the liquid, the polarised light has been

turned through a certain angle. The rotation is progressive, and hence will depend upon the length of the substance through which the light has to pass. It is possible to turn the plane of polarisation through several revolutions if the length of substance is great enough.

Certain liquids rotate the plane of polarisation of light to the right, and are called dextro-rotatory. Others rotate it to the left, and are called lævo-rotatory. It should be mentioned that this property is not confined to pure liquids and solids, but also applies to solutions.

The amount of rotation is easily measured by means of an instrument called a polarimeter, which makes use of the facts explained above. It consists essentially of two Nicols, which can be rotated with respect to each other, *i.e.*, one is fixed, and the other can be rotated. Between the two Nicols there is a space into which can be fitted a tube containing the liquid under examination. These tubes are made of definite lengths, 5 cm., 10 cm., 20 cm. and 25 cm., so that the length of liquid through which the light passes is known. For a complete description of the instrument the practical text-books should be consulted.

The apparatus is set up without the tube of liquid, and a beam of monochromatic light is passed through the instrument. This may be sodium light, or one of the mercury lines may be used. The light passes through the polarising prism, called the polariser, and falls on the second prism called the analyser. The analyser is turned until there is complete darkness, and the reading of the scale is taken. Now the tube of liquid is inserted. On looking through the analyser, the field now appears bright, because the liquid has rotated the plane of polarisation, and the analyser is now no longer at right angles to the vibrations of the beam. It has to be turned through a certain angle for complete darkness again to be reached. This is the angle through which the plane of polarisation has been rotated. Modern polarimeters have numerous improvements over the simple type, the essentials of which are described above.

Besides depending upon the length of the substance through which the light has to pass, the rotation α, depends upon the density of the substance, the temperature, and the wavelength of light used.

The specific rotatory power of a pure liquid is given by the equation

$$[\alpha]_D^t = \frac{\alpha}{ld}$$

where $[\alpha]_D^t$ is the specific rotatory power at a temperature t, and for light of the sodium D line, l is the length of the column of liquid in decimetres, and d is the density in grams per c.c.

For a solution, the concentration is substituted for density and the equation becomes

$$[\alpha]_D^t = \frac{\alpha}{lc}$$

The concentration c is expressed in grams per c.c. of solution.

The molecular rotation is given by

$$[M]_D^t = \frac{M\,[\alpha]}{100}$$

where M is the molecular weight.

110. Optical Activity and Chemical Constitution.—Optical activity is bound up with asymmetry of the molecule or crystal structure. Thus, if an organic compound has an " asymmetric " carbon atom, it is optically active, and exists in two distinct forms, or more. One form is dextro-rotatory, the other lævo-rotatory to the same extent. A third form, consisting of a mixture of the other two in equimolecular proportions also exists, which can be separated by various means into the two optically active components. Such a substance is said to be " externally compensated." Sometimes, a fourth form is known, which, although optically inactive, is not a mixture of the optically active forms because it cannot by any means be resolved into those forms. This form is called " internally compensated," and exists where there are two or more asymmetric atoms in the molecule. An example of this is given by tartaric acid.

By an asymmetric carbon atom we mean one that is joined to four different atoms or groups. Thus, the compound

$$\begin{array}{c} CH_3 \\ | \\ H—C^*—OH \\ | \\ COOH \end{array}$$

known as lactic acid, has an asymmetric carbon atom, indicated by the asterisk. It exists in three forms, two optically active, and a third " racemic " or externally compensated mixture.

For further details of this important subject a text-book on organic chemistry should be consulted.

As mentioned above there is a type of optical activity not dependent upon the molecule, but upon the arrangement of molecules in a crystal. The effect is best shown by quartz.

(b) Magnetic Rotation

111. Methods of Observation.—If a beam of polarised light is passed through a transparent substance placed in the field of an

electromagnet, so that the light travels in the direction of the lines of force, the plane of polarisation is rotated. This must not be confused with ordinary optical activity. It is a general effect, and is shown by all transparent substances, not only those having an asymmetric carbon atom. This magnetic rotation will be dependent upon the direction of the lines of force, so that by means of a suitable apparatus it is possible to reflect the light back upon itself, and thus increase the rotation. The angle of rotation, ω, is proportional to the length, l, of substance used, and also to the strength of the magnetic field, H. Hence

$$\omega = \phi l H.$$

The constant ϕ is called Verdet's constant. It has been found that this varies with the nature of the substance, the wavelength of light used (Wiedemann), and the temperature, though the influence of temperature on magnetic rotation is small.

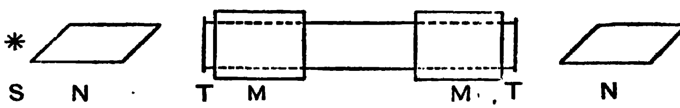


FIG. 78.—Magnetic Rotation. S = source of light, N, N = nicol prisms, M, M = poles of electromagnet, T, T = tube containing substance.

The application of magnetic rotation to the study of the structure of organic compounds was first carried out by W. H. Perkin. The method of determining magnetic rotation is a comparative one, so that it is not necessary to work with absolute units. Water is taken as the standard substance. If the same apparatus is used every time a determination is made, there is no need to introduce the length of the tube, the temperature, or the wavelength of the light used. To compare the effect of equal masses of different liquids, it is only necessary to divide the observed rotation by the density. The rotation in unit length of tube, α, divided by the density d, is called the relative specific magnetic rotation, r,

$$r = \frac{\alpha}{d}.$$

The relative molecular magnetic rotation is given by

$$r_M = \frac{M\alpha}{md} = \frac{M\alpha}{18d},$$

where M is the molecular weight of the substance, and m is the molecular weight of water.

The absolute molecular magnetic rotation, R_M, can readily be found by multiplying the right-hand side of the equation by the

absolute value for water, which has been found by Rodger and Watson to be 0·01312 minutes of arc at 20° C.

$$R_M = \frac{0{\cdot}01312\ M\alpha}{18d} \text{ minutes of arc.}$$

112. Magnetic Rotation and Structure.—Since isomeric substances give different values for the molecular magnetic rotation it is clear that the property is not merely additive but is also constitutive. It is impossible to give a detailed list of the results obtained here; all that can be done is to mention briefly some of them.[1]

It has been found that geometrical isomers have a different magnetic rotation, the "trans" modification possessing the greater, as a rule. Optical isomers also differ in magnetic rotation, but only slightly.

Thus,

Ethyl maleate	9·625
Ethyl fumarate	10·112
Ethyl tartrate	8·766
Ethyl racemate	8·759
Glucose	6·723
Galactose	6·887

From the consideration of a large number of observations on different homologous series, Perkin arrived at the value 1·023 for the CH_2 group. A list of values for the different groups has been drawn up, but it is necessary to add a "series constant," which varies with the series to which the substance belongs, when computing the magnetic rotation of a compound. Thus, the series constant for the fatty acids is 0·393, for the normal paraffins it is 0·508, and for ketones 0·375.

The method has been useful in deciding structures, *e.g.*, in cases of keto-enol tautomerism (acetoacetic ester), and was applied by Perkin to the study of the terpenes.

(c) Refractivity

113. Formulæ for Refractivity.—As a result of work begun in 1858, Gladstone and Dale proposed that, when comparing the refractive indices of substances, the density should be eliminated, as the refractive index is largely influenced by this. They therefore used the formula

$$n - 1$$

[1] For a detailed account, and list of values, see Cohen, "Organic Chemistry," Vol. II. (Arnold), pp. 45–56.

r is called the specific refractive index, or the specific refractivity; n is the refractive index, and d the density.

In 1880, a second formula was put forward simultaneously by H. A. Lorentz, of Leyden, and L. Lorenz, of Copenhagen. This was

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}.$$

This formula is independent of pressure and temperature, whilst that of Gladstone and Dale is not. It is now the usually accepted formula, although that of Gladstone and Dale is still sometimes used. Whilst the latter is simply empirical, the Lorentz and Lorenz equation was derived from considerations of the Clerk Maxwell electromagnetic theory of light.

The molecular refractivity (M) is obtained by multiplying the specific refractivity by the molecular weight (m) of the substance :—

$$M = \frac{n-1}{d} \,.\, m \text{ or } M = \frac{n^2 - 1}{n^2 + 2} \,.\, \frac{m}{d},$$

Refractive index is usually determined by the refractometer. Pulfrich's refractometer is the one most frequently used. There is no space for a description of the instrument here; the practical text-books should be consulted. With a good instrument the refractive index can be determined to the fourth decimal place, so that the determination of refractivities is a matter of great accuracy. The value, of course, varies with the wavelength of the light employed, which must always be specified.

114. Refractivity and Constitution.—Refractivity is additive, but also constitutive. It has been found that similarly constituted isomers have the same refractivities ; *e.g.*, the figures for isopropyl alcohol and propyl alcohol are 17·44 and 17·42 respectively (using light of the hydrogen α line, H_α). The values for butyl iodide and isobutyl iodide are exactly the same, 33·25. It seems reasonable, then, to assume that spatial differences do not make a great effect on the refractivity. However, differences have been found among geometrical isomers, but not among optical isomers.

By studying the refractivities of a number of homologous series, the value for CH_2 was found to be 4·57. The table on p. 266 gives the values obtained for some elements and groupings.

Ring formation seems to exert little influence, at any rate, where the members of the ring exceed four in number. A peculiar point is that the value for the double bond varies with the arrangement of the double bonds in the compound. A compound containing conjugated double bonds, *i.e.*, the grouping —C=C—C=C—, has a higher refractivity than that calculated from the ordinary constants. This "exaltation," as it is called, is characteristic of compounds

TABLE XLIX

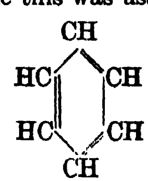
		H_α
Carbon	C	2·414
Hydrogen	H	1·092
Oxygen	O′ (enol)	1·522
,,	O < (ethers)	1·639
,,	O″ (keto)	2·189
Chlorine	Cl	5·933
Bromine	Br	8·803
Double bond =		1·686
Triple bond ≡		2·328

containing the conjugated double bond. When two double bonds occur together, *i.e.*, when they are cumulated, there is also a difference in the value.

TABLE L

	$M\alpha$. Obs.	$M\alpha$. Calc.	Difference.
(Isolated) Diallyl, $CH_2 : CH.CH_2.CH_2.CH : CH_2$	28·77	28·78	− 0·01
(Cumulated) Valerylene, $(CH_3)_2C : C : CH_2$	24·34	24·18	+ 0·16
(Conjugated) Isodiallyl, $CH_3.CH : CH.CH : CH.CH_3$	29·87	28·78	+ 1·09
(Twice conjugated) Hexatriene, $CH_2 : CH.CH : CH.CH : CH_2$	30·58	28·28	+ 2·30

It is to be noted that optical exaltation has not been observed in benzene, although it would appear to have a series of conjugated double bonds. At one time this was used as an argument against



the Kekulé formula in favour of the centric formula, but it has since been shown, on comparison with other ring compounds containing a conjugated system, that benzene is no exception to the general rule.

The property of refractivity has been useful in providing evidence for the formulæ of some compounds belonging to the terpene and camphor class, and also in studying the phenomenon of dynamic

isomerism such as exists in keto-enol isomerism as typified by aceto-acetic ester, $CH_3CO.CH_2COOC_2H_5$.

$$CH_3.CO.CH_2.COOC_2H_5 \rightleftharpoons CH_3.C(OH):CH.COOC_2H_5.$$

The results have not, however, proved entirely trustworthy. Calculations of the quantities of the two forms present in the equilibrium mixture based on refractivity do not agree with those obtained by chemical or other physical means. Hantzsch has also applied refractivity to the study of salt formation with the pseudo acids.

(d) Absorption of Light

Although not strictly a property of liquids alone, the study of light absorption, as far as it concerns chemical constitution, is best taken here. Further mention of this subject will be made in the chapter on Photochemistry (Chapter XIX).

115. Absorption Spectra and their Determination.—When a beam of white light is passed through a prism it is broken up into its constituent colours, owing to the variation of the refractive index of the glass for different coloured lights, a spectrum being formed. If now some transparent substance, solid, liquid, or gas, is placed in this spectrum, certain parts of the spectrum will be absorbed, and where this occurs dark bands, known as absorption bands, will appear. Thus, if a substance absorbs orange light, this part of the spectrum will be reduced in intensity in the light which has passed through the substance. We say that the substance has an absorption band in the orange.

Absorption bands are studied by means of an instrument called a spectrophotometer, which will give in addition to the position of the bands their relative intensities. This work can be done either visibly or with a camera. The Hilger spectrophotometer will be described. The essential parts are shown in the diagram. Light from a source A, consisting of an arc between iron-tungsten electrodes, passes by one path through a prism P, then through the rotating sector S, of which the aperture can be varied, and then on to a biprism B and in to the spectrograph G. A second beam passes through the cell D containing the liquid under examination, through the prism P′ which is exactly similar to P, through a sector of fixed aperture, and biprism and into the spectrograph, the two beams being analysed side by side. The only difference between the paths of the two rays is that the first does not pass through the liquid, but passes through an aperture of which the size can be varied, whilst the second passes through the liquid and through an aperture of fixed size. Now the arc gives a great number of lines well spaced out through the spectrum. Those following the first

path have no absorption, but certain parts of the spectrum will be more or less absorbed from the rays following the second path by the liquid. The two spectra are photographed side by side, using various apertures for the first ray. The closing of the aperture reduces the intensity of the comparison spectrum. When at any wavelength the intensity of the unabsorbed ray is equal to the intensity of the absorbed ray, the opening of the aperture gives a measure of the amount of absorption at that wavelength.

It will have been noticed that in the Hilger spectrophotometer just described, the comparison beam is reduced in intensity until it is equal to that passing through the absorbing medium. This can be accomplished in several ways. In the instrument described, which was the earliest with which quantitative results were obtained,

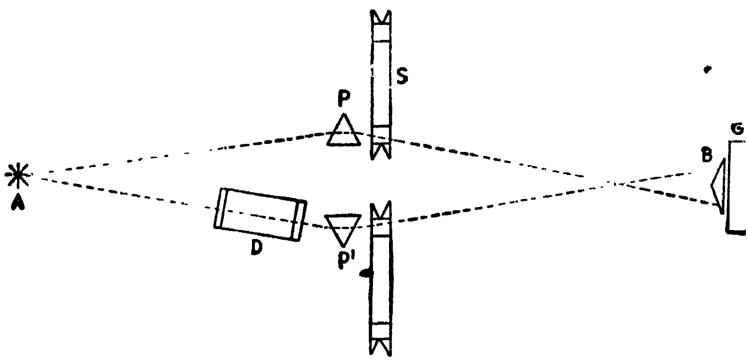


FIG. 79.—Spectrophotometer (diagrammatic).

the duration of intermittent exposures was varied. In others, polarisation is used, and in the Spekker spectrophotometer the aperture of the light-path is varied. Otherwise the principles are the same. In ultra-violet work it is, of course, necessary to employ quartz instead of glass throughout.

In some modern instruments the photo-electric cell is used as a detector for the light, the strength of current produced being a measure of the intensity of the light.

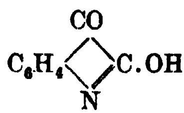
116. Absorption Spectra and Chemical Constitution.—The relationship between colour and chemical constitution is a question which cannot be studied here.[1] It is our purpose to note some examples of the use of the absorption spectrum in helping to decide questions of constitution.

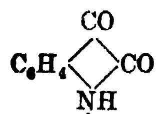
In the first place it must be said that at present we have no

[1] See Chapter XIX, § 361, and Cohen, "Organic Chemistry," Vol. II. (Arnold), Chapter II.

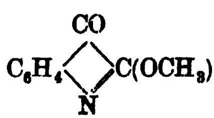
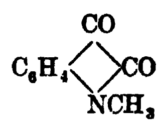
method of stating *a priori* what the absorption spectrum of a given compound is going to be like. The only way in which the absorption spectrum can be used is by a comparative method. It has often been found that substances of similar constitution have similar absorption spectra (Hartley's rule). For example, all the permanganates in solution show similar absorption bands; methyl and ethyl esters usually have very similar absorption spectra, and so on. Hence if it is found that two substances have similar absorption spectra, it is usually safe to say that they also have similar constitutions. In this way the study of absorption spectra has proved of considerable value in deciding questions of structure.

A few examples may be taken. First of all, consider the substance isatin, the oxidation product of indigo. This almost colourless substance may, according to its chemical properties, be regarded as possessing a lactim or a lactam structure. The two formulæ are given below.


Lactim.


Lactam.

Two isomeric methyl derivatives of isatin are known. Their formulæ are

 and 

It is known that the introduction of a methyl group into a molecule makes very little difference to the absorption spectrum. The absorption spectrum of the second methyl derivative resembles that of isatin very closely. Hence it argued that isatin has the formula II, *i.e.*, it has the lactam structure.

This method has also been of use in the determination of the structure of the alkaloids, such as cotarnine and hydrastine.

Hartley, Dobbie, and Lauder studied keto-enol tautomerism by this means, and were able to show, by comparing its absorption spectrum with that of its methyl ether, that phloroglucinol, which sometimes acts as a phenol and sometimes as a ketone, exists entirely in the phenolic form in the free state.

There are many other cases of the use of absorption spectra in deciding constitution, but for these the larger text-books or monographs should be consulted.

F. The Molecular Weights of Liquids

117. The Determination of the Molecular Weight of a Liquid.—It is a matter of some difficulty to determine the molecular weight of a liquid. Whilst the molecular weight of a vapour or a gas is readily determined by finding its density and applying the corrected Avogadro Hypothesis, no such method is available for the determination of the molecular weight of a substance in the liquid state. In order to do this it is necessary to make use of some of the properties already mentioned.

One method is to make use of the equation of Ramsay and Shields (§ 102), connecting molecular surface energy with temperature.

$$\left[\frac{M}{D}\right]^{\frac{2}{3}} = k\,(T_c - T - 6).$$

The value of k for a number of liquids was found to be 2·12, and as so many gave this value, it was assumed that these were normal liquids. Some liquids, however, give a value for k less than 2·12, and these are supposed to be associated, *i.e.*, their molecular state consists of aggregates of simple molecules. If x is the degree of association (*i.e.*, the aggregates consist of x simple molecules), then Mx is the molecular weight of the substance, and presumably, if this is used instead of M, the Ramsay and Shields' equation should be obeyed. Hence

$$\gamma\left[\frac{Mx}{D}\right]^{\frac{2}{3}} = 2{\cdot}12\,(T_c - T - 6).$$

Thus x can be found.

In this way, the molecular weight of water has been shown to agree with the formula $(H_2O)_3$ at certain temperatures. The molecular complexity decreases as the temperature rises, as is shown in the accompanying table. At 60° C. water would appear to be $(H_2O)_3$; at 20° C. it is clearly a mixture of $(H_2O)_3$ and some higher molecular aggregates.

By this method a number of liquids have been found to be associated as shown in the Table II on p.271.

Table LI.—(I.)—Degree of Association of Water

0	20	40	60	80	100	Temp. ° C.
3·81	3·55	3·18	3·00	2·83	2·66	x

(II.)—ASSOCIATION OF LIQUIDS

Substance.	Temp. Interval. °C.	Degree of Association.
Methyl alcohol	16–78	3·43–3·24
Ethyl alcohol	16–78	2·74–2·43
Acetic acid	16–132	3·62–2·77
Phenol	46–184	1·42–1·18
Phosphorus	78–132	3·76
Sulphur	115–160	6·00
Nitrogen dioxide	2–20	2·02
Sodium nitrate	300–400	10·68
Potassium nitrate	341–407	8·73

Some objections have recently been made concerning the use of the Ramsay and Shields' equation for this purpose. Some observers urge the approximate nature of the Ramsay and Shields' equation, but a far more important objection is that brought forward by Dutoit and Mojoiu. The surface tension measures conditions at the surface of a liquid and not in its interior. It has been shown by Gibbs and others that these surface conditions are quite abnormal. Thus, in dealing with a solution, the concentration of solute is not the same at the surface as in the bulk of the liquid. Hence it is justifiable to assume that there may be a difference of molecular weight at the surface of a liquid, and this would be the one measured by the Ramsay and Shields' equation. It cannot be argued that if a liquid is associated at the surface it will be associated in the interior of the liquid.

A further objection is the fact that it is definitely known that certain liquids which would not be expected to be associated give values for k which are somewhat removed (both above and below) from the value 2·12.

The general conclusion is, therefore, that it is not safe to argue about the actual degree of association from the Ramsay and Shields' equation, though it may be used to show the existence of association from the qualitative point of view.

Several other methods of deciding whether a liquid is associated or not are based on surface tension. The parachor has already been referred to (p. 248). It will be remembered that this constant is defined by the equation

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{(D - d)}$$

which involves the molecular weight. If the constituent groups of

the molecule of a compound are known, its parachor can be calculated from the table of constants which has been drawn up. The parachor can also be found from the above equation. If the two values agree, the substance is normal; if not, it is abnormal. Unfortunately this method requires the knowledge of the constitution of the substance before anything can be done, and hence is of little use for determining the molecular weight of an unknown liquid.

Most normal liquids obey Trouton's Rule, which states that

$$\frac{Ml}{T} = \text{const.} = 21,$$

where M is the molecular weight, l the latent heat of evaporation, and T the boiling point of the liquid on the absolute scale. Abnormal liquids deviate considerably from this rule. However, the rule is not sufficiently accurate to enable a direct determination of the molecular weight to be made.

The Molecular Volume, which is an additive property, may be used in a similar way to the parachor to find out whether a liquid is associated, but it is not of any use in determining the amount of association. The structure of the substance must be known, when the molecular volume can be calculated from the list of constants drawn up. The molecular volume can also be derived by experiment. A comparison of the two will give some idea as to whether the liquid is normal.

Sometimes certain physical properties of a liquid give a hint as to their complexity. If we take water as an example we find that it contracts on heating from 0° C. to 4° C., but above this temperature it expands. It is clear that near this temperature, 4° C., there is some alteration in the equilibrium between the liquid molecules.

Ramsay and Young's rule concerning the boiling points of related liquids may be used for detecting association (see p. 237).

It was also remarked in connection with viscosity that the ratio

$$\frac{d}{M} \cdot \eta \times 10^6,$$

where d is the density, η the coefficient of viscosity, and M the molecular weight (apparent), comes out between 40 and 60 for normal liquids, whereas for associated liquids the value is considerably higher. This can be used as a criterion of association (§ 108).

118. Some Properties of Associated Liquids.—Many of the liquids which have been shown by various methods to be associated, are found to possess certain properties in common.

In the first place, associated liquids frequently contain the hydroxyl group. The reason why association takes place when

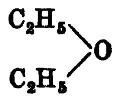
this group is present is probably because the OH group possesses both donor and acceptor properties (§ 61). It can therefore co-ordinate with itself. The association, where it exists in these cases, depends upon the presence of both the hydrogen and the oxygen of the hydroxyl, for if one of them is absent the liquid behaves normally. Thus, ether $(C_2H_5)_2O$, which contains only the oxygen, is not abnormal; ethyl alcohol is. The compound $C_2H_5.H$ or ethane, is normal.

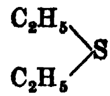
It is found that associated liquids fall into two classes; those where the association factor appears to be limited to two, and where the limit is nearly reached at comparatively low concentrations, when the substance is dissolved in non-associating solvents; and those where the association factor is much higher, but the association is much less in dilute solution. Examples of the first class are the carboxylic acids, and of the second the alcohols and phenols. The carboxylic acids, such as acetic, seem never to be associated to aggregates containing more than two simple molecules, whereas the alcohols and phenols form larger aggregates.

Associated liquids are usually miscible in all proportions with each other, but not with normal liquids; similarly normal liquids are usually completely miscible with each other, but not with associated liquids. Thus the associated liquids water and ethyl alcohol are miscible in all proportions; the normal liquids ether and benzene are completely miscible, but water and benzene are not miscible.

Associated liquids have all the properties of co-ordinated compounds, as would be expected if the theory that association is due to the presence of both donor and acceptor properties in the molecule is true. Especially do they possess low volatility and high dielectric constants.

If water were a normal liquid, its boiling point would be very much lower than it is. It is known that the ethers boil at temperatures about 60° C. lower than the thio-ethers. The latter compounds are related to the former by the fact that they are ethers, the oxygen of which has been replaced by sulphur.


Ether.


Thio-ether.

Now, if we apply this to the case of water, we find that sulphuretted hydrogen boils at − 60° C. Hence water should boil at − 120° C., if it were normal. Its true boiling point is, of course, 100° C., 220° C. more than that calculated on the assumption that it is

normal. We are therefore justified in saying that it is an abnormal liquid, and that it is much less volatile than it would otherwise be.

The table below gives the dielectric constants of some compounds. It is noticed that those of suspected associated liquids are considerably greater than those of normal liquids. Nitrobenzene and acetic acid are exceptions.

TABLE LII

Associated Liquids.		Normal Liquids.	
Water	82	Carbon tetrachloride	2
Formic acid	58	Acetic anhydride	21
Methyl alcohol	33	Benzene	2
Acetamide	59	Ether	4
Acetic acid	6	Nitrobenzene	36
Ethyl alcohol	27	Carbon disulphide	3
Amyl alcohol	16	Chloroform	5
Glycerol	39	Ethyl acetate	6

Associated liquids are found to be good ionising solvents. This is partly due to their high dielectric constant which weakens the attractive forces between the ions and facilitates their separation.

119. Structure of Liquids.—It is frequently stated in the recent scientific literature that extremely small traces of substances profoundly influence the properties of a liquid. An example of this is the problem of intensive drying (see p. 330) in which a very small amount of water can bring about vast changes in the properties of a liquid. If this is true it seems necessary to assume that liquids have a certain structure like solids, but to a less marked degree. Solids possess a crystal structure—a definite arrangement of atoms and molecules which characterises the solid. Until recently it has been supposed that liquids possess no such structure, but that their molecules are in random motion.

If a minute trace of an added substance can make such a profound alteration of properties, in which it must be supposed that the molecules of added substance exert forces quite beyond their normal molecular range, it is clear that these forces must be transmitted in some way or other by the molecules of liquid, presumably by some electrical polarisation (Chapter XX.). This would not be possible unless liquids possess a structure through which these forces could be transmitted. The forces certainly could not be transmitted through molecules moving with random motion, unless

some other mechanism entirely were assumed—viz., activation (§ 171), and the kinetics of the problem forbids this, as there is insufficient energy to cause activation.

If liquids do possess a structure it would be expected that they would exist in different forms, as allotropes. This always becomes a possibility when a fixed structure is assigned. From discontinuities in curves showing the connection between the vapour pressure, density, specific heat, viscosity, and dielectric constant of certain liquids, and temperature, it has been inferred that there are two liquid forms of nitrobenzene, carbon disulphide, and ether. It may be mentioned that two liquid forms of helium have recently been described, with a transition point depending on the pressure.

It has now been shown that a number of liquids do possess a definite structure. Considerations of density, the fact that the viscosity of a liquid varies with temperature in quite a different way from gases, and the determination of the dielectric constants of polar liquids at various frequencies have led to this view. Moreover, work on *X*-ray diffraction in liquids (§ 125) confirms this fact. The properties of water are compatible with this liquid possessing a "pseudo-crystalline" structure, as proposed by Fowler and Bernal.

SUMMARY

The properties of liquids which have been dealt with have been :—

A. *Vapour Pressure.*

B. *Molecular Volume.*—This is mainly an additive property, *i.e.*, it depends upon the component atoms, and very little upon their arrangement. If it were strictly additive, it would depend entirely upon the atoms present and not at all on the way in which these are combined. Constitutive properties are those which depend largely upon the structure of the molecule. It may be mentioned that there is only one strictly additive property, and that is mass.

Certain properties are independent of the nature of the atoms present or of the way in which they are combined, but depend only upon the number of them present. Such are the vapour pressures of solutions, to be dealt with in a later chapter, which are the same for solutions containing the same number of solute molecules in a given volume of solution. These are called colligative properties.

C. *Surface Tension.*—It is the effect of temperature on surface tension that is of the most importance in connection with constitution. The value of k in the Ramsay and Shields' equation gives information as to the association or not of a liquid (with certain reservations). The most important application of surface tension, however, is in the derivation of the parachor, which has been of very great use in deciding questions of structure, and in providing evidence in connection with the electronic theory of valency.

D. *Viscosity.*—This property is partly additive, and partly con-

stitutive, but actually has served little purpose in the investigation of liquids.

E. *Optical Properties.*—(*a*) *Optical Activity.*—This property enables one to discover whether a compound of carbon (or of other elements, such as Sn, Si) has an asymmetric molecule.

(*b*) *Magnetic rotation* is a universal property, and is not possessed only by those substances containing an asymmetric atom. This property is partly additive and partly constitutive, and has been extremely useful.

(*c*) *Refractivity.*—This property, again, is partly additive and partly constitutive, and has been used considerably to discover the structures of isomers.

(*d*) *Absorption of Light.*—The absorption spectrum enables us to determine constitution by a comparative method. The rule of Hartley, that analgous compounds have analogous absorption spectra, is useful.

F. *Molecular Weight of Liquids.*—There is no satisfactory method for determining the molecular weight of a liquid. Many liquids appear to be associated (*i.e.*, to consist of aggregates of molecules). The evidence for association may be obtained (1) by using the equation of Ramsay and Shields for the variation of molecular surface energy and temperature; (2) by using the parachor; (3) by applying Trouton's rule; (4) from observations of molecular volume; (5) by applying Ramsay and Young's rule concerning the boiling points of related liquids; (6) from Dunstan's viscosity rule.

Associated liquids frequently contain the (OH) group, which possesses both donor and acceptor properties. They possess low volatility and high dielectric constants. They are good ionising solvents.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 10.—Determination of the critical temperature of carbon dioxide.

Procure a thick walled capillary tube containing some liquid carbon dioxide. Place it in a water bath, and gradually raise the temperature of the water until the boundary between liquid and gas just disappears. Take the temperature of the water.

Experiment 11.—Effect of pressure on the boiling point of a liquid.

Fit up an apparatus for distillation of water *in vacuo*, complete with manometer. Reduce the pressure, and take the boiling point of the water in the usual way, reading the manometer at the same time. Allow a little air to enter, and again determine the boiling point. Do this at intervals up to atmospheric pressure.

Experiment 12.—Determine the molecular volume of ethyl acetate.

The instructions for this are given on p. 242. The most difficult part of this experiment is filling the bulb-tube.

Experiment 13.—Compare the surface tensions of water and benzene.

Use the drop weight method described on p. 245. Make sure the apparatus is quite clean before attempting a determination. If the surface tension of water is known (72 dynes per cm. may be taken as a rough figure), the absolute surface tension of benzene may be calculated.

Experiment 14.—Determine the viscosity of benzene.

Use the viscometer described on p. 258. Find the viscosity of water from the tables, and work out the absolute viscosity of benzene.

SUGGESTIONS FOR FURTHER READING

YOUNG, S. "Stoichiometry." (*Longmans.*)
COHEN, J. B. "Organic Chemistry," Vol. II. (*Arnold*, 1924.)
SMILES, S. "Relations between Chemical Constitution and Physical Properties." (*Longmans.*)
FRIEND, J. N. "Text Book of Physical Chemistry," Vol. I. (*Griffin*, 1932.)

QUESTIONS

(1) Show how the critical temperature and pressure can be calculated from van der Waals' equation.

(2) How may the critical pressure, temperature and volume of a gas be determined ?

(3) Write an essay on the liquefaction of gases, pointing out the chief methods available, and the principles upon which they are based.

(4) What properties of liquids may be made use of in determining chemical constitution ? Describe the experimental work necessary in the investigation of any one of these properties.

(5) In what ways does a knowledge of surface tension assist in deciding chemical constitution ?

(6) By what methods may the molecular condition of a liquid be investigated ?

(7) What do you understand by the term "association" ? What types of liquids are associated ? Indicate how the degree of association may be determined.

(8) Calculate the molecular viscosity of propionic acid $C_2H_5.COOH$ from the data given on p. 259. The observed value was 630.

(9) Calculate the parachors of the given substances from the data on p. 249. The observed values are given in brackets. (*a*) Ethylene ($CH_2 = CH_2$) (99·5) ; (*b*) acetone ($CH_3.CO.CH_3$) (161·5) ; (*c*) nitrosyl chloride ($Cl - N = O$) (108·1).

(10) The following data are known for the fluorides of sulphur, selenium and tellurium :—

	Density of Liq., *D*. gm./c.c.	Density of Vapour, *d*. gm./c.c.	Surface Tension γ. dynes/cm.
SF_6	1·975	0·009	13·78
SeF_6	2·340	0·011	13·71
TeF_6	2·67	0·013	13·23

Find the parachors of the fluorides.

(11) The viscosity of nitromethane is 0·00627 poise at 25° C. Its density is 1·1312. The formula is CH_3NO_2. What conclusions do you draw as to its molecular complexity in the liquid state?

(12) The viscosity of nitrobenzene ($C_6H_5NO_2$) is 2·0380 centipoises at 19·50° C. Its density is 1·2. Is this liquid simple, or associated?

CHAPTER VII

THE CRYSTALLINE STATE

120. Characteristics of Solids.—When a gas is cooled or submitted to pressure it becomes liquid, and in this state the molecules are much more closely packed than they are in the gaseous state. They have not the freedom of motion that they enjoy in the form of a gas, and thus a liquid is much more difficultly compressible than a gas. If a liquid is cooled it becomes crystalline, possessing even smaller compressibility than before. Indeed, now the molecules have very little capacity for motion, arranging themselves in a definite order which gives rise to the crystalline structure of the solid.

It was thought until recently that all solids were crystalline, and that there were no truly amorphous solids. Many solids which appear to be amorphous are, in fact, supercooled liquids. Glass is one of these. Some workers have considered such substances as members of a distinct state of matter, called the vitreous state. However, Riley has recently obtained truly amorphous carbon (*J. C. S.*, 1946, 456), and it would therefore seem that the solid state must include both crystalline and amorphous substances.

Every crystalline substance is made up of an assembly of smaller units all having the same geometric form. Although a crystal is quite homogeneous, it possesses different properties in different directions, and is therefore said to be *anisotropic*.[1] Thus, crystals conduct heat and electricity better in one direction than in another. The index of refraction may vary in different directions in a crystal.

Much information is now available concerning the arrangements of molecules and atoms inside the crystal. Such arrangements determine crystalline form, and are described later (§ 125).

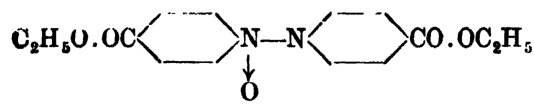
121. Liquid Crystals.—Crystals are usually regarded as possessing a certain rigidity, by reason of which they are called solids. Yet, there are a number of substances in which the weakness of the crystal forces results in lack of rigidity. These are called "*liquid crystals.*" They will actually flow, and will rise up a capillary tube, showing that the surface forces which result in surface tension are strong enough to overcome the weak crystal forces. These substances are not intermediate between the two states—liquid and crystalline. It is merely a question of the weakness of the crystal forces, which are not sufficiently powerful to support a definite

[1] Cubic crystals (§ 124) are fully symmetrical, and are therefore isotropic.

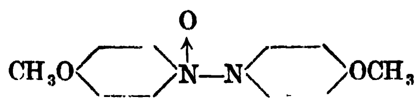
geometrical form. In order to avoid the confusion which might arise from the use of the name "liquid crystals," the term "*mesomorphic state*" has been used.

Liquid crystals possess a definite melting point at which they become true liquids, and are doubly refracting. Examples of substances which can form liquid crystals, of which some three hundred are known, are :—

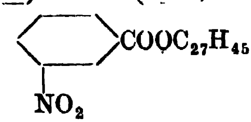
ethyl para-azoxybenzoate



p-azoxyanisole



cholesteryl m-nitrobenzoate



cholesteryl acetate $CH_3COOC_{27}H_{45}$

ammonium oleate $C_{17}H_{33}COONH_4$.

When the solid substance giving liquid crystals is heated it appears to melt at a given temperature, forming a cloudy liquid which shows anisotropic properties, as mentioned above. The cloudy liquid represents the mesomorphic state. Some substances have been examined by means of *X*-ray analysis (§ 125) in the liquid-crystal state, and faint indications of crystalline structure have been obtained.

The effect of a magnetic field on the liquid-crystals is interesting. Substances in the mesomorphic state are turbid, but when a magnetic field is applied they become clear, in the direction of the lines of force. The explanation of this, as well as of the double-refraction shown by liquid-crystals, probably lies in the arrangement of the molecules. Vorländer has pointed out that all substances which are capable of existing in the mesomorphic state have long or flat molecules. This would be expected from an examination of the formulæ given above. It may be supposed that when one of these substances is melted, the cohesion between the molecules, which previously held them in the crystal arrangement, does not break down uniformly in all directions. There may be a lateral cohesion which still exists, which will tend to hold the molecules together in bundles. This makes the liquid anisotropic. The properties may be expected to be different in different directions, for rudimentary

crystals still exist. When the magnetic field is applied, all these bundles orient themselves in the same direction, along the lines of force, and the liquid clears in this direction.

The viscosity of liquid crystals is small, whereas that of liquids with heavy molecules is usually large. It is evident, then, that the peculiar properties of the mesomorphic state are not due to mere polymerisation.

When a solid which can exist in the mesomorphic state is heated it changes into that state at a definite temperature, called the transition point. Then, on further heating, the mesomorphic state disappears, and the true liquid state takes its place. The temperature at which this occurs is the melting point. Thus, for *p*-azoxyanisole, the transition point is 118·3° C., and the melting point 135·9° C.

122. The Process of Crystallisation.—From the point of view of theory, it is a fairly simple matter to draw a picture of what happens when crystallisation takes place. In a liquid the molecules are moving with random motion. They possess all sorts of velocities—some very high (molecules possessing these escape from the surface as vapour), and others below the average. Those molecules with low velocities obviously have a kinetic energy below the average, and when they happen to come together more or less in a certain arrangement corresponding to the crystalline form of the substance, the forces which hold the crystal together are strong enough to keep the molecules together. They may remain together for some time, or they may meet a molecule moving with high velocity, and therefore possessing high kinetic energy. This molecule, on collision, causes them to separate. Consider now a liquid which is cooling. Here the kinetic energy of the molecules is getting less and less, for heat is being given out, and hence the conditions for long life of the crystal nucleus are more advantageous. Finally, when the liquid cools sufficiently, the crystal forces are strong enough to overcome the bombardment by molecules which have too great a velocity to be added to the crystal nucleus, and the liquid crystallises. The crystal nucleus has the power of attracting other molecules to it by virtue of the crystal forces, and it forms a trap for all molecules which do not possess sufficient energy to escape. So the crystal grows.

When a crystal is heated, the reverse change may be supposed to take place. The molecules are gaining energy, which gives them a greater vibration in the crystal arrangement, which is called the crystal lattice. Finally they gain sufficient energy to break down the crystal lattice, overcoming the crystal forces, and the crystal melts.

It must be understood that the molecules are always oscillating in fixed mean positions in the crystal lattice, but they have not the power of translational motion. Sometimes, however, a molecule may oscillate so violently that it breaks away from the crystal and goes directly into the vapour state. This explains why a crystal has a vapour pressure.

It is clear that heat will be required to give the molecules sufficient amplitude of oscillation to break down the lattice. This is the heat that is commonly referred to as latent heat of fusion. It is taken in when a substance melts, and is given out when it solidifies from the liquid state.

The above is merely a theoretical picture of the crystallisation process. In practice the way in which crystals are formed, and the significance of crystal forces are still little understood. Some work on this subject has been done recently by Tammann, who points out that there are two definite processes involved in crystallisation. They are first, the formation of the crystal nuclei, and second, their growth. Each process must be studied separately.

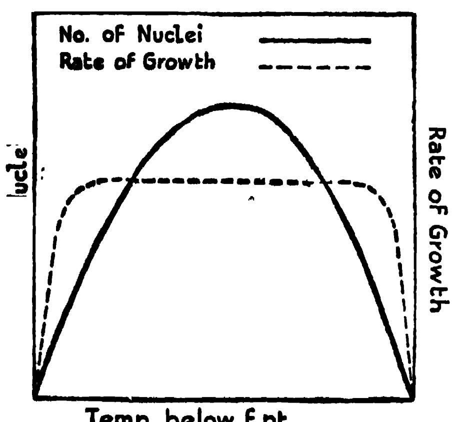


FIG. 80.

It has been found possible to count the number of crystallisation nuclei formed when a liquid is cooled and supercooled under various conditions. It has been shown that the number of nuclei increases with decrease of temperature as this is reduced below the freezing point, passes through a maximum, and then decreases. If the number of nuclei formed is plotted against the temperature a curve of the type shown in Fig. 80 is obtained. It is clear that this is a typical probability curve, so that the formation of nuclei is governed by probability.

It has also been found that the rate of formation of nuclei is dependent to a great extent upon the presence of dust particles, and upon mechanical agitation. Indeed without the presence of these, supercooling usually occurs.

Turning to the other side of the matter—the rate of growth of the crystal once the nucleus has made its appearance—it has been found,

as a result of the work of Gernez and of Tammann and his pupils, that this increases at first with decrease of temperature, then remains constant over a considerable temperature range, and finally falls rapidly. If the conditions are such that there is slow formation of nuclei and rapid growth, a few large crystals will result. If, on the other hand, the conditions are favourable to the growth of a large number of nuclei, but slow growth of crystals, there will be a large number of small crystals.

The study of the growth of crystals, particularly as regards their form during this period, shows that they undergo continual change. A perfect crystal is best made by very slow growth, during which a number of facets, in the usual course of events never seen, appear and disappear.

Spangenburg and Neuhaus (1928) turned a sphere from a single crystal of rock salt, and then suspended it in a solution of sodium chloride. The crystal grew or diminished in size according to whether the solution was slightly supersaturated, or slightly unsaturated. The concentration of the solution was carefully kept constant by addition of salt or water, and the slow development of faces by the sphere was noted. Ultimately a polyhedron developed. The speed of growth of the various faces was found. They did not all develop at the same rate.

Bound up with the formation of crystals, is the dissolution of crystals. It is of interest to know how a crystal is attacked by a solvent; whether certain faces disappear first, or whether the crystal dissolves as a whole. Little work appears to have been done in this direction, although Traube has shown that dissolution takes place at definite points on the crystal surface, and a cellular structure is thereby formed. Immediately before the crystal dissolves it breaks down into particles which are so small that they can be seen only under the ultra-microscope (§ 335). In this work, a cinematograph film was taken showing the process of dissolution. The results are considered to be in agreement with Smekal's theory that a crystal is made up of blocks of a few molecules, called "lattice blocks," which are separated by canals or pores. When a crystal dissolves it first breaks up into these blocks. This theory has been used also to explain the contamination of crystalline substances by impurities derived from the mother liquor. It is a well-known fact that crystalline substances are frequently impure, and this is a matter of importance when dealing with precipitates in quantitative analysis. Precipitates such as barium sulphate frequently contain adsorbed impurities which are difficult to wash out. It may be that these are adsorbed in the hypothetical pores which exist in the crystal. The hygroscopic nature of some crystals has also

been ascribed to the same cause, water being adsorbed in the pores.

With reference to the effect of impurities on crystals, it may be mentioned that in some instances crystals reject impurities. For example, many dyes are not taken up by crystals, and it is possible to crystallise a colourless substance from a solution that has been artificially coloured by certain dyes. This is not always so, however, and if an impurity can form a solid solution with the crystal, or, if it is adsorbed in the pores, it is a matter of some difficulty to remove it.

Sometimes the crystalline form of a solid may be completely altered by the presence of impurities in the solution from which it is deposited. It is possible to obtain cubes of alum although the usual crystal habit is octahedral.

123. Supercooling and Amorphous Substances.—It has already been stated that when a melt is cooled it frequently does not crystallise without the presence of dust particles, or crystallites (small crystals) of the substance to be crystallised, or mechanical agitation. A liquid in this condition is said to be supercooled. The way in which the presence of dust particles causes precipitation is not known. The other methods of bringing the melt to crystallise can be given some theoretical explanation. The presence of crystallites actually provides the nuclei, whilst mechanical agitation provides further opportunities for the molecules of the liquid to come into those arrangements from which crystalline nuclei result.

Supercooling is most frequently found with viscous liquids. When such a liquid is supercooled its already high viscosity gradually increases, and, of course, this means decreased motion of the molecules, since the internal friction is increased. Hence, as supercooling proceeds, the chance of crystal nuclei appearing becomes less and less, and a glass (which actually is still a liquid) is frequently produced. This flows like a liquid, though, of course, very much more slowly, owing to the much increased viscosity, and no new phase appears during the cooling.

A typical example of a supercooled liquid is ordinary glass. It flows, as can be seen if a piece of glass rod or tubing is supported on two pegs, about a metre apart, when it will soon show a permanent sag. Old glass, too, will crystallise out when rendered slightly less viscous by warming, making it useless for glass-blowing. This process is known as devitrification.

Many substances, especially when thrown down as precipitates, appear to show no definite crystalline form to the naked eye, or even under the microscope. These are usually called amorphous substances. It has now been shown that almost all substances

previously thought to be amorphous, are in fact microcrystalline, or else are liquids. Thus the so-called "amorphous" phosphorus (red phosphorus) has been shown to consist of minute crystals, invisible to the naked eye, and not shown under the microscope, but definitely indicated by X-ray diffraction (§ 125). The question is not, however, definitely settled. Some maintain that the amorphous state should be regarded as a fourth state of matter. Recent work has shown that certain metals can be obtained in thin layers (by vaporisation and subsequent condensation, or by other methods) in such a form that they are almost non-conductors of electricity. X-ray investigation of these layers (§ 130) shows them to possess no definite crystalline structure, and they are probably amorphous.

Sometimes a precipitate is obtained in a gelatinous form when two reactants are mixed. For example, the precipitate of aluminium hydroxide, when ammonia is added to a solution of aluminium chloride, is gelatinous, and troublesome to filter. On examination by the X-ray method it is found to possess no definite crystalline structure. When, however, the hydroxide is obtained as a powder by prolonged warming with ammonia it shows a crystalline structure. It is clear that the gelatinous aluminium hydroxide cannot be called a supercooled liquid, so these results seem to provide evidence for the existence of a separate amorphous state. As already stated (§ 120) Riley and his school have obtained truly amorphous carbon.

124. Crystal Systems.—It is necessary to have an idea of the elements of crystallography if the study of crystals is to be of any value. What is given here is the merest outline. For more detailed study text-books of crystallography should be consulted.

Although crystals of a given substance may vary in size, and in the development of the different faces, due to variations in the method of preparation, the angles between the faces are always the same. This is called the *law of the constancy of interfacial angles.*

If three convenient axes are taken in the crystal, say three axes mutually at right angles, the faces will cut these axes at definite points (Fig. 81). The distances of these points from the point of intersection of the axes, O (called the origin), are called intercepts. The second law of crystallography is concerned with these intercepts. It is found that if the axes are suitably chosen, the intercepts of the faces upon them bear a simple ratio to each other, or particular faces may cut an axis at infinity (*i.e.*, the face may be parallel to the axis). This is called the *law of rationality of intercepts* (or indices), and will be illustrated below. It forms the basis of a system of nomenclature for the crystal faces.

A crystal is made up of an innumerable set of smaller crystals, but if broken up, a point would be reached at which the smallest possible crystal of the substance would exist. If it were broken down still further the crystal would be completely destroyed, and the molecules which made up the crystal would be obtained. This being so, it is clear that this smallest possible crystal has the same degree of importance as the molecule.

It has been known for some time that a crystal must be made up of an ordered assemblage of units. The only way in which the crystal can be made up of these units is such that if a definite point (*e.g.*, the centre of gravity) is taken in each unit, these points must lie on lines and planes which divide the space into a set of parallel-sided cells. The sides of these cells are parallel to the crystal axes mentioned above. The cell is called the *unit cell*, and the assemblage of points is called the *space lattice*.

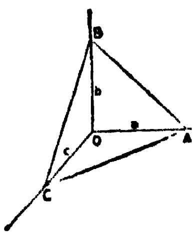


FIG. 81.—Intercepts, *a*, *b*, *c*, made on the axes OA, OB, OC.

The unit cell will be completely defined by the ratio of the edges, and the interfacial angle. These are shown in Fig. 82 as *a*, *b*, and *c*, and as α, β, and γ respectively. Of course, these figures can be determined from larger crystals. It is not necessary to measure the size of the crystal unit, for each larger crystal is made up of a number of smaller ones, and hence the ratio remains the same. An example is copper sulphate, for which the following figures are given :—

$$a : b : c = 0{\cdot}5715 : 1 : 0{\cdot}5575$$

$$\alpha = 82^\circ\ 16' \qquad \beta - 107^\circ\ 26' \qquad \gamma - 102^\circ\ 40'$$

It may be said that this diagram does not resemble a copper sulphate crystal. It is quite true that in external form it does not, but the method of obtaining it must be remembered. It is the unit obtained by joining the points, arbitrarily chosen, in the tiny crystals of which the larger crystal is composed, and so its shape may bear no relationship to the actual shape of the crystal, apart from the fact that its edges correspond to the crystal axes.

Crystals usually possess certain elements of symmetry. These can be divided into planes of symmetry, axes of symmetry, and a centre of symmetry. A plane of symmetry divides a crystal into two portions each similar to the other. If a crystal of chrome alum, which has the octahedral form is taken (Fig. 83), it is seen that there are several planes of symmetry, two of which are marked in the figure.

An *axis of symmetry* is an axis about which rotation of the crystal causes it to occupy the same position more than once during the rotation through 360°. The position may be taken up twice, thrice, four times, and so on, the axis being called accordingly an axis of twofold, threefold, and fourfold symmetry, respectively.

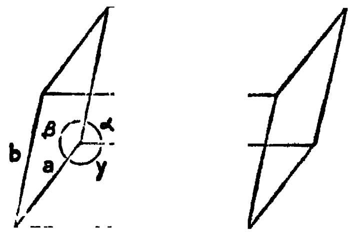


FIG. 82.—Unit cell.

A crystal has a *centre of symmetry* when like faces are arranged in pairs in corresponding positions on either side of this centre.

The cube has the greatest symmetry. It can readily be shown from a diagram that it has thirteen axes of symmetry (three of these are of fourfold, four of threefold, and six of twofold symmetry), nine planes of symmetry, and a centre of symmetry, making altogether 23 elements of symmetry.

Of course, only a perfect crystal shows all the elements of symmetry possible for its form. Most crystals are imperfect and have some faces better developed than others, but as mentioned before, the angles between the faces are the same whether the crystal is perfect or imperfect.

To fix a face of a crystal it is customary to define it by the intercepts it makes on certain chosen axes (p. 285). Thus, in fixing the faces of the cube, three lines mutually at right angles passing through the centre of symmetry would be chosen as axes. These are shown in Fig. 84 below.

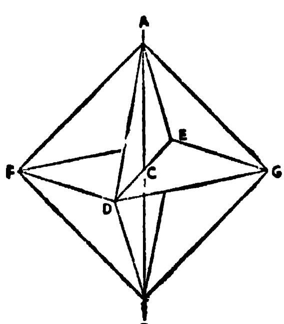


FIG. 83.—Chrome alum crystal showing two of the planes of symmetry (ADBE, FDGE), an axis of symmetry (AB), and a centre of symmetry (C).

The centre of symmetry is O. The three lines taken at right angles are OK, OL, OM. The line OK cuts the face ABCD at X; the line OL cuts the face ABJH at Y, and the line OM cuts the face ADGH at Z. These faces are not cut by these axes anywhere else; except when the axes are produced backwards, when they cut the opposite faces. It is clear that the intercepts OX, OY, and OZ are all equal and can therefore be taken as unity. The faces are defined by the intercepts they make on the axes. Thus, face ABCD cuts the X axis at the point 1, the Y axis at infinity, and the Z axis at infinity. Hence

this face can be represented as (1, ∞, ∞). More often the reciprocals of the intercepts (called indices) are used, so that the face becomes the (1, 0, 0) face. The face FGHJ has similar indices to ABCD, since it is the mirror image of the latter. The plane ABJH cuts the X axis at infinity, the Y axis at 1, and the Z axis at infinity. Its name is therefore the (∞, 1, ∞) face, or the (0, 1, 0) face. The face ADGH cuts the X axis at infinity, the Y axis at infinity, and the Z axis at 1. It is therefore the (∞, ∞, 1) face, or the (0, 0, 1) face.

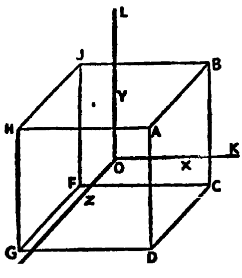


FIG. 84.

In this way the faces of any crystal can be defined. The axes chosen for the calculation need not be axes of symmetry, though they are usually chosen thus. It has been found that these indices are always small numbers, below 7.

The octahedron (Fig. 85) may be taken as another simple example. Take, as before, three axes mutually at right angles passing through the centre of symmetry C. Since the triangles which make up the faces of this figure are all equilateral, the intercepts CX. CY, and CZ are all equal. The face AXY is therefore the (111) face. In fact, all the faces of the octahedron have these same indices.

It has been found that all crystals can be referred to seven different types of structure. They are all modifications in one way or another of seven simple types. These are given in Table LIII, together with their axial characteristics and elements of symmetry. The fact that there are seven bases of crystal structure does not mean that there are only seven different kinds of crystal form. Few substances exist in the simplest forms; there are usually a number of extra faces. Thus, the octahedron belongs to what is called the cubic system, because it has the same type of axes as the cube.[1]

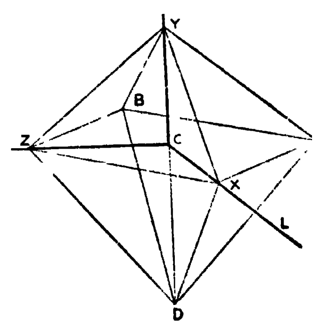


FIG. 85.

125. The Structure of Crystals.—When light falls on an object which is of the same order of size as the wavelength of light, it does not form a perfect shadow, but is

[1] Good photographs of crystals of the various systems are given in "Inorganic and Theoretical Chemistry," F. Sherwood Taylor (Heinemann).

TABLE LIII.—CRYSTAL SYSTEMS

System.	Axial characteristics.	Symmetry.	Substances typical of system.
1. CUBIC	Three equal axes at right angles.	Nine planes. Thirteen axes.	Sodium chloride. The alums. Diamond. Many metals. Fluorspar.
2. TETRAGONAL	Three axes at right angles, two only being of equal length.	Five planes. Five axes.	Potassium ferrocyanide. Zircon. Rutile. Tinstone.
3. ORTHORHOMBIC	Three axes at right angles, but all of different lengths.	Three planes. Three axes.	α-Sulphur. Iodine. Potassium nitrate. Barytes.
4. TRIGONAL	Three axes not at right angles, but of equal length and making equal angles with each other.	Three planes. Four axes.	Quartz. Graphite. Sodium nitrate.
5. HEXAGONAL	Three axes of equal length in one plane, making angles of 60° with each other, and a fourth axis at right angles to them, and not of the same length.	Seven planes. Seven axes.	Lead iodide. Magnesium. Beryl.
6. MONOCLINIC	Three axes of unequal length, one at right angles to the other two, which are inclined at an angle not 90°.	One plane. One axis.	Potassium chlorate. Borax. Sodium carbonate. Gypsum. β-Sulphur.
7. TRICLINIC (or anorthic).	Three axes of unequal length, all inclined at unequal angles, not a right angle.	No planes. No axes.	Copper sulphate. Potassium dichromate. Orthoboric acid. Microcline.

diffracted. This fact is investigated by means of a diffraction grating, which consists of a number of very fine lines drawn on metal or some other material. When monochromatic light falls on a

diffraction grating, the light is diffracted and a number of images are formed, called the first, second, third, etc., order images. The fine lines act as small obstacles in the path of the light and cause it to be diffracted. For further information on this point, the text-books of physics must be consulted.

In 1912 Laue suggested that if *X*-rays were actually light of very small wavelength, and if crystals were made up of orderly arrange-

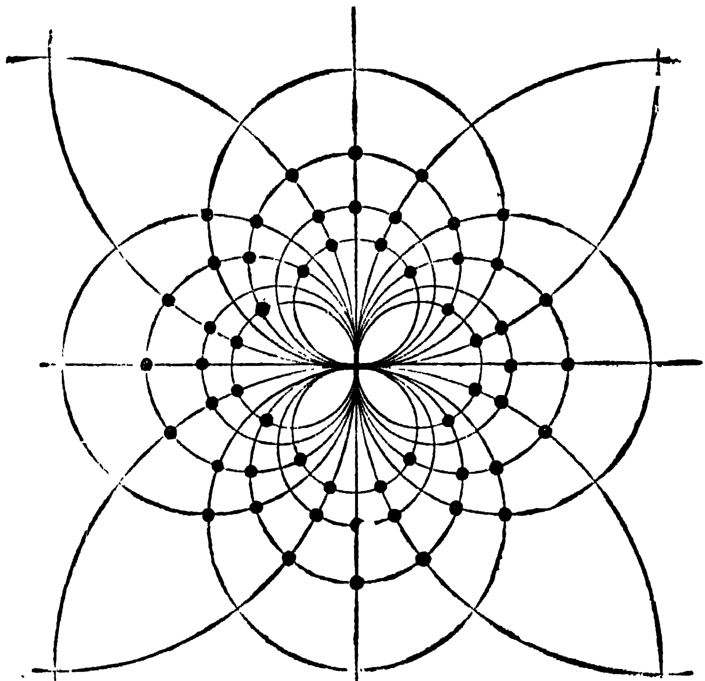


FIG. 86.—Theoretical Diffraction Pattern for Sodium Chloride. (After Fig. 8, from Dr. E. S. Hedges' *Chapters in Modern Inorganic and Theoretical Chemistry* (Edward Arnold & Co).)

ments of atoms or molecules, then the crystal should act as a diffraction grating for *X*-rays. This orderly arrangement is the crystal lattice, or space lattice (p. 286). The spaces between the molecules in a crystal had been roughly computed to be about 10^{-8} cm., and this is of the order of the wavelength of *X*-rays. The crystal would not be such a simple diffraction grating as the type used in physics. It would, of course, be a three-dimensional grating. However, the fundamental effect, it was thought, would be the same. Laue showed, from a theoretical point of view, that if a beam of *X* rays were to fall on a crystal, it should be transmitted through

the crystal as a number of diffracted beams. If a photographic plate were arranged directly behind the crystal, these beams should make their appearance on the plate as a number of spots. From a consideration of the position of these spots it should be possible to arrive at some conclusions about the positions of the molecules in the crystal.

The experimental work in connection with this was carried out almost immediately by Friedrich and Knipping. Their results agreed completely with the predictions of Laue. The points are found at the intersection of circles, which represent the diffraction at the various planes. Fig. 86 shows the theoretical X-ray diffraction pattern of rock salt.

This method did not receive a great deal of attention, since at the time little was known about the nature of X-rays and the arrangements of atoms and molecules in crystals, although this research

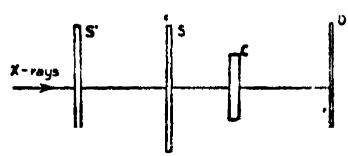


FIG. 87.—Diagram to illustrate the Laue experiment. X-rays are passed through pin-holes in the lead sheets S′ and S″, then through the crystal C. The beam is diffracted and a number of images of the pin-holes appears on the plate D, their positions being defined by the intersection of circles of radii dependent upon the distances between the lattice planes.

did much to increase our knowledge on both these points. The method has, however, been used very extensively since.

A little later Sir W. H. and W. L. Bragg suggested that a crystal should be used as a reflection grating rather than as a transmission grating. The arrangement of atoms or molecules in a crystal is such that the atoms and molecules may be regarded as occurring in planes which are fixed by the symmetry of the crystal. The faces of a crystal are parallel to these planes containing the atoms or molecules, and those faces which occur most frequently are developed parallel to those planes in the space lattice which contain the largest number of atoms or molecules. When X-rays fall on these planes they are reflected, and the resultant reflected beams interfere with each other, just as when a beam of light falls on a pile of glass plates, as in the echelon grating. The theory of this is very easily followed.

In Fig. 88 the lines aa', bb', cc', dd', etc., represent the planes of atoms or molecules parallel to a face of the crystal. According to

our hypothesis, these planes are all parallel and are equidistant. Suppose that the distance between them is d W represents an advancing wave-front. The first plane is struck at A, and the wave is there reflected along AB. The angle WAa is equal to the angle $BAa' = \theta$. Part of the beam, however, is reflected at the second plane, at the point E, part at the third plane, and so on. The line WE is produced to C. The perpendicular to the crystal planes from A must meet it at C. AD is drawn perpendicular to EC. From the geometry of the figure it is clear that the angle $DAC = \theta$. The beam which emerges from the crystal along AB is made up of a number of beams which have travelled through the crystal for different distances, and therefore will be out of phase unless the path is a finite integral number of wavelengths different. Thus, for

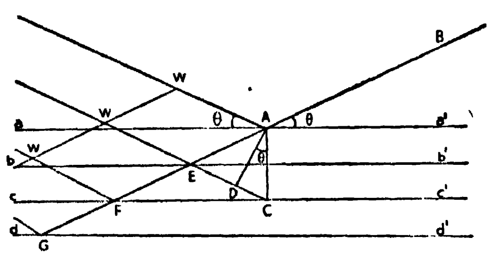


FIG. 88.

reinforcement, the path difference must be an integral number of wavelengths; for interference the path difference must be an odd number of half wavelengths. We wish to express the first of these conditions mathematically.

The path difference of the waves taking the courses WA and WE is

$$EA - ED = \Delta.$$

But, $\quad EA = EC.$

Therefore, $\quad \therefore \; EC - ED = DC = \Delta$

But, $\quad DC = AC \sin\theta = 2d \sin\theta,$

where d is the distance between successive planes.

For maxima, Δ must equal $n\lambda$, where λ is the wavelength and n is an integer. Hence the condition for maximum reflection is

$$n\lambda = 2d \sin\theta.$$

It is clear that it is necessary to know λ and θ to find d. n is known from the order of the spectrum, or, if monochromatic light is used, the order of the reflection. The first reflection is obtained when $n = 1$. At first the wavelengths of X-rays were not known, so that it was necessary to express the distances between the planes

in the crystal lattice in terms of λ. This was, of course, suitable for comparative work, but not until the wavelengths of the X-rays were found was it possible to give an absolute measure of the lattice constants.

The apparatus used by the Braggs for the investigation of crystals was very much like an ordinary spectrometer in principle, and is shown in Fig. 89.

X-rays are generated from the X ray tube A, and are made as far as possible monochromatic by passing through absorbing screens S, after which they pass through lead slits L, to obtain a fine beam. The beam passes on to the crystal face, the crystal being mounted on a turntable which can be moved over a scale V, very much as a diffraction grating is mounted in ordinary spectroscopy. The reflected beams are passed into an ionisation chamber D, which is connected with an electrometer. The ionisation chamber can also be moved over a circular scale independently from the crystal. The chamber contains some easily ionisable gas, such as sulphur dioxide, and when the gas is ionised by the rays a reading is obtained on the electrometer. The crystal face and the ionisation chamber are rotated about their common axis, the chamber being rotated through twice the angle through which the crystal is turned. In this way the angle between the face and the ionisation chamber, and the face and the incident beam, are kept the same. The strength of ionisation produced at different angles, as measured by the current indicated by the electrometer, is determined and plotted, and from the graph the maxima are obtained.

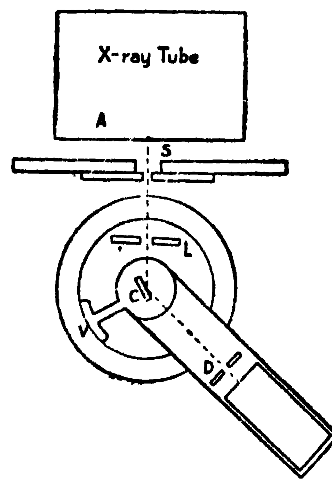


FIG. 89.—X-ray Spectrometer.

These maxima should be governed by the equation

$$n\lambda = 2d \sin \theta,$$

so that, since d and λ are constant for any one face, the ratios of $\sin \theta$ should be small whole numbers.

The curves obtained for potassium chloride (sylvine crystals) and sodium chloride (rock salt) are given in the accompanying figure. The angles given in the top scale of Fig. 90 are the settings of the

ionisation chamber, and are equal to 2θ, where θ is the angle through which the crystal is turned.

For sodium chloride, the maximum reflections for the (100) face

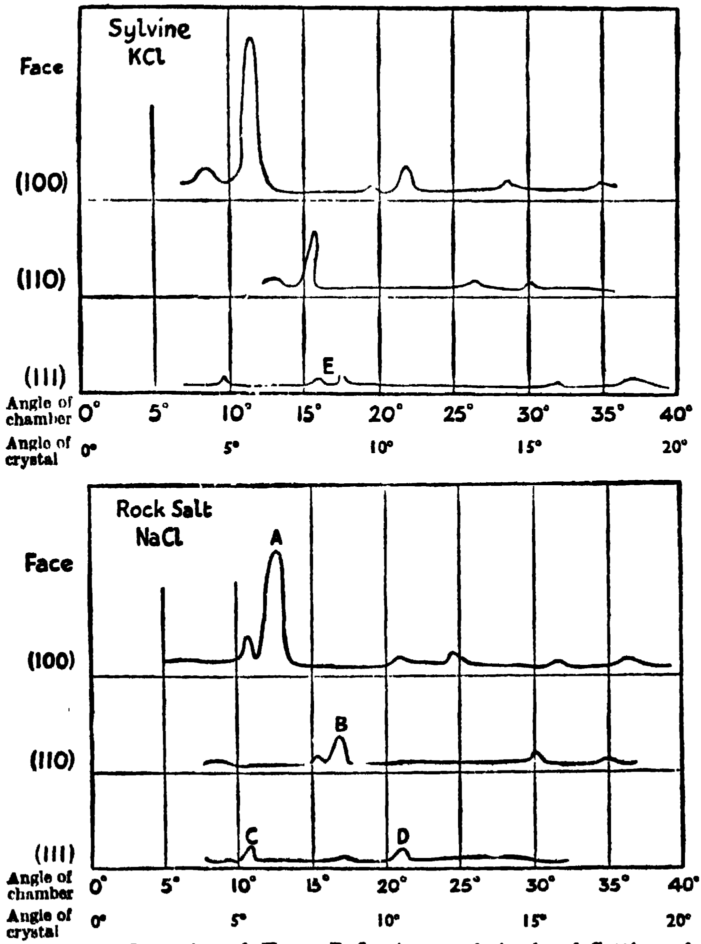


FIG. 90.—Intensity of X-ray Reflections and Angle of Setting of Ionisation Chamber for Sylvine and Rock Salt (Bragg).

occurred at $\theta = 5{\cdot}9°$, $11{\cdot}85°$ and $18{\cdot}15°$ for palladium X-rays. The sines of these angles are 0·103, 0·205 and 0·312, which are very nearly in the ratio 1 : 2 : 3. This speaks for the truth of the relationship derived (p. 292).

These figures enable the distance between the planes in the space lattice parallel to this face to be calculated. In the equation

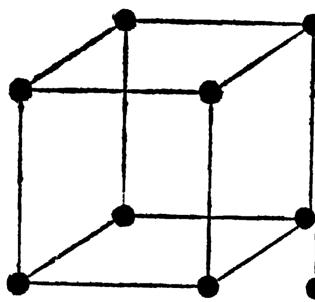
$$n\lambda = 2d \sin \theta,$$

when $n = 1$, $\sin\theta = 0{\cdot}103$. Hence

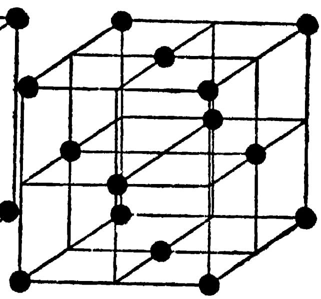
$$\lambda = 2d\,(0{\cdot}103) \qquad \therefore\ d = 4{\cdot}85\lambda.$$

Thus we have the distance between the reflecting planes of particles parallel to the (100) face in terms of the wavelength of the rays used.

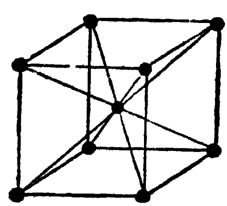
In order to find the absolute spacing, it is necessary to decide to which system the crystal belongs, and then to calculate the relative distance between the planes in the different types of lattice that are



(a)
Simple cubic lattice.



(b)
Face-centred cubic lattice.



(c)
Body-centred cubic lattice.

FIG. 91.—Types of Cubic Lattice.

possible for the different faces. These are compared with the results of the X-ray analysis, and the correct space lattice is thus arrived at. Once this is done, the absolute spacing can be derived from a knowledge of the density of the crystal and Avogadro's number. The crystal could then be used as a means of determining the wavelength of X-rays, just as an ordinary diffraction grating is used for the determination of the wavelength of light.

These points are clearly brought out in the study of the crystals sylvine and rock salt. These were the first crystals that were successfully studied by the Braggs, and they are comparatively simple It is well known that they both crystallise in the cubic

system, for which there are three space lattices possible, which are called the simple cubic, the face-centred cubic, and the body-centred cubic lattices. These are shown in the diagrams on page 295.

The simple cubic lattice has one structural unit, whatever that may be in the crystal under consideration (molecule, atom or ion), at each corner of the cubic cell. In the face-centred lattice there is a structural unit at each corner, and one at the middle of each face of the cell, whilst in the body-centred lattice there is one unit at each corner, and one at the centre of the cube. Sylvine and rock salt may crystallise in one of these three ways. The relative spacings between the planes containing structural units, and which act as reflection planes for the rays, are now calculated. The possible crystal faces are (1) parallel to the cube face (100), (2) perpendicular to the diagonal of the face (as in the faces of a dodecahedron) (110), and (3) perpendicular to the cube diagonal (as in the octahedron) (111). The relative spacings are given in the table below, and should be verified by the student.

TABLE LIV

Type of Lattice.	(100).	(110)	(111)
Simple cubic . . .	1	$\frac{\sqrt{2}}{2}$ (·707)	$\frac{\sqrt{3}}{3}$ (·577)
Face-centred cubic . .	1	$\frac{\sqrt{2}}{2}$ (·707)	$\frac{2\sqrt{3}}{3}$ (1·154)
Body-centred cubic . .	1	$\sqrt{2}$ (1·414)	$\frac{\sqrt{3}}{3}$ (·577)

Consider the curves obtained for the intensity of reflections against the angle of setting of the ionisation chamber (Fig. 90). For sodium chloride, we see that the first order reflections occur at the following angles of crystal face for the different faces

A (100) 5·9°
B (110) 8·4°
C (111) 5·2°.

It must be remembered that small deviations in the curve cannot be counted as reflections, and that the maxima will occur at double these angles if we consider settings of the ionisation chamber, since

this has to be moved through twice the angle that the crystal is turned through in order to receive the reflection. To make this clear, the first order maxima are marked in the diagram with the letters A, B and C. The sines of these angles and other data are given in the table

$$n = 1$$

$$d = \frac{n\lambda}{2 \sin \theta}.$$

TABLE LV

Face	(100)	(110)	(111)
Angle (θ)	5·9°	8·4°	5·2°
sin θ	0·103	0·146	0·094
d	4·854λ	3·425λ	5·319λ
Ratio of d	1	0·706	1·096

These ratios of d obviously agree with the face-centred cubic lattice, and with no other, so it is clear that in rock salt the ultimate crystal cell has its structural units arranged in a face-centred manner. The difficulty now arises as to what the structural unit is. If it is the NaCl molecule, presumably there will be some distance between the two atoms in the molecule, and we may associate the centre of gravity of the molecule with the points of the lattice. Thus, the Na and Cl atoms will actually lie on two face-centred cubic lattices, which are separated from each other by a definite distance (the distance between the atoms in the molecule), and interpenetrate. The same result is arrived at if we associate with the points of the lattice the sodium atoms. The chlorine atoms will, as before, lie on a similar interpenetrating lattice. However, it is now universally regarded that the units are sodium and chlorine ions, not atoms. The problem now is to find the position of these two face-centred cubic lattices with respect to each other. The clue to the solution of this problem is found in the intensity of the various order reflections. The X-rays are scattered by the structural units, and the amount of scattering will be proportional to the mass of the scattering particle. The heavier the atom (or structural unit, whatever it may be) the greater will be the intensity of the reflection. The chlorine is considerably heavier than the sodium, so that the

reflections will be mainly due to it, those due to sodium being much weaker.

It is found that if it is supposed that the chlorine space lattice is displaced from the sodium space lattice half-way along the side of the fundamental cube, the results shown in the reflection curves are accounted for. The type of lattice thus obtained is shown in Fig. 93. It is noticed that the sodium and chlorine ions alternate. The lattice is now made up of eight simple cubic lattices, but containing two kinds of ion. The planes parallel to the cube faces contain the same number of chlorine and sodium ions, and the spacing is identical with the original fundamental space lattice. This is also the case for the (110) planes. However, the original

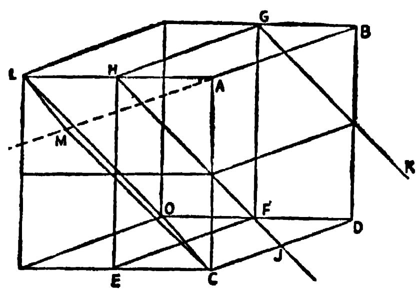


FIG. 92.—Diagram showing the planes referred to in the text.
The planes ABCD, EFGH are (100) planes.
The plane GHJK is a (110) plane.
The plane LMCO is a (111) plane.
Note that these are alternately made up of sodium and chlorine ions, and are half as far apart as they would have been if the sodium and chlorine ions had not been arranged in this manner.

(111) planes are now alternated with planes containing sodium ions only at half the distance between the original planes. It is obvious that the presence of these planes will interfere with the reflections from the (111) faces. For the reflections from the two successive chlorine planes to reinforce each other, the path difference must be one wavelength. When this is so, any rays reflected from the sodium planes will have travelled odd numbers of half wavelengths, and so will be 180° out of phase. If the reflections from the chlorine and sodium planes therefore were equal in intensity, there would be no reflection at all at this angle. However, the sodium is not so heavy as the chlorine, and consequently the reflections from the chlorine planes are more intense than those from the sodium planes, and there is a resultant effect, though it is much weaker than it would otherwise be. This is true for the first order reflection, and

PLATE III.—X-RAY POWDER DIAGRAM OF THE HYDROCARBON $C_{22}H_{46}$.
(By permission of Messrs. Adam Hilger Ltd.)

[To face p. 298.

explains why this is extraordinarily weak. For the second order reflection the waves from the sodium planes would be one wavelength behind those from the preceding chlorine planes, and so there would be reinforcement. For the third order reflections, however, we have similar conditions to the first, the waves from the sodium planes being one and a half wavelengths behind those from the preceding chlorine planes. This agrees with the intensities obtained. In Fig. 90, C is the first order, D the second order, whilst the third order spectrum is not sufficiently intense to mark.

When a crystal of potassium chloride is considered, it is found to possess a similar lattice to that of sodium chloride, but here the first order spectrum for the (111) face has entirely disappeared. This is easily explained on the above basis. Chlorine and potassium are very close in atomic weight, and hence the intensity of X-rays reflected from them will be approximately the same. Here the waves will neutralise each other completely for the first and third order reflections, whilst they will reinforce each other for the second, giving a more powerful reflection of the second order, shown at E, Fig. 90.

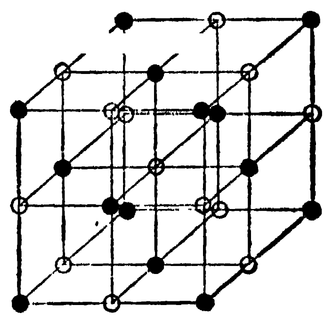


FIG. 93.—Sodium Chloride Lattice.

It is interesting to carry the investigation further and find the exact distance apart of the planes. This can be done if the dimensions of the unit cell can be found. It has already been seen that the elementary cell of the sodium chloride crystal consists of a chlorine ion at each corner, and one at the centre of each face. Each atom at a corner of the cube really belongs at the same time to seven other cubes, so that only one-eighth of its mass may be regarded as belonging to the elementary cell. There are eight of these atoms, so that the resultant total mass of atoms at the cube corners is 1. Every atom in a cube face is shared with another cube, so that it gives half its mass to any particular elementary cell. There are six of these, so that they give the mass of three ions altogether to the elementary cell. The total mass of chlorine ions is therefore four. It can be shown in a similar way that the number of sodium ions in the cube is equivalent to the mass of four. The cell therefore contains four molecules of sodium chloride. The density of sodium chloride crystals is 2·17, and the molecular weight 58·454.

The gram-molecular volume is, therefore, 58·454/2·17 = 26·93 c.c. This must contain a number of molecules equal to Avogadro's number, *i.e.*, $6{\cdot}06 \times 10^{23}$. The volume associated with four molecules will be

$$4 \times \frac{26{\cdot}93}{6{\cdot}06 \times 10^{23}} = 177{\cdot}8 \times 10^{-24} \text{ c.c.}$$

This must be the volume of the unit cell. The cube root of this gives the length of the side of the cube, and this comes out to be $5{\cdot}623 \times 10^{-8}$ cm. One Ångstrom is 10^{-8} cm., so that the length of the side is 5·623 Å. The distance between the (100) planes is half this, *i.e.*, 2·811 Å. The other distances can be calculated in a similar way. Knowing this distance between the planes, it is clear that the crystal can now be used to determine the wavelength of the *X*-rays used.

The *X*-ray spectrograph differs from the *X*-ray spectrometer just described in fixing the positions of the maximum reflections photographically instead of by an ionisation chamber. The Laue method is a typical one involving the spectrograph. The arrangement of apparatus for this method has already been described, and the type of photograph explained. The spectrographs are easily obtained if a good crystal is available, but the interpretation of the diagrams is not easy, and is usually accomplished by means of gnomonic projection. The method cannot be described here. Laue photographs find their main use in the determination of the symmetry and correct unit cell of a crystal. Qualitative data are obtained from complicated planes far more numerous than in any other diffraction methods, and these can be employed with great certainty in the fixing of the unit cell.

126. X-ray Powder Spectroscopy.—Debye and Scherrer (1916) and Hull (1917) suggested that a powder might be used instead of a large crystal in *X*-ray spectroscopy. If the crystal is replaced by a thin film of crystalline powder an entirely different pattern is formed. If the small crystals are present in large enough numbers and if they are arranged in a disordered fashion, two conditions which are almost invariably fulfilled, there are bound to be some of them which are in a position to reflect from every system of atomic planes whose spacing is more than a certain minimum, fixed by the wavelength of the *X*-rays used.

The substance is powdered and made into a rod and placed at the centre of a circular camera. The beam of *X*-rays, after suitable treatment by slits, is passed through a hole in the photographic film on to the specimen. The *X*-rays are diffracted in such a way as to give a series of cones with their apices at C (Fig. 94) Where they cut the

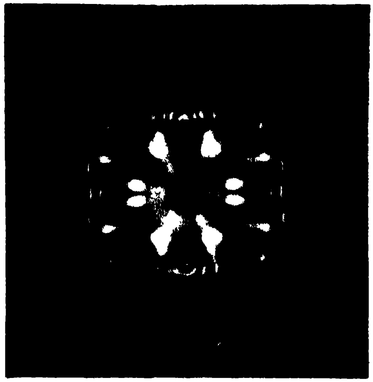


PLATE IVa.—X-Ray Rotation Photograph of Stearic Acid.
(By permission of Messrs. Adam Hilger Ltd.)

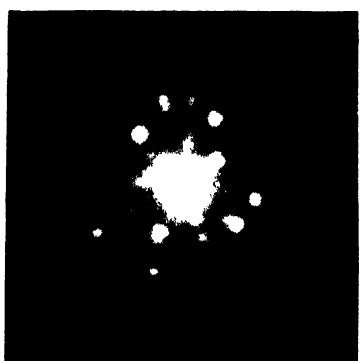


PLATE IVb.—Laue Photograph of a Single Crystal of Sodium.
(By permission of Messrs. Adam Hilger, Ltd.)

[To face p. 300.

film, the circular sections of the cones will be made evident. When the film is unrolled the photograph is of the form shown in Plate III., which is the photograph obtained for $C_{22}H_{46}$. It will be clear from what has been said above that the apparently straight lines in this diagram are really portions of arcs.

Each line in this photograph arises from comparatively few crystals—just those in fact which are oriented in such a way as to reflect the rays from one particular plane—and so they will be much weaker than the spots in the Laue diagram unless a considerably more powerful source of rays is used.

It is clear that this method has advantages over the other methods. In the first place, crystals can be studied which it is not possible to obtain large. Whereas it is difficult to grow large crystals of most substances, anything can be finely powdered. The intensities of the reflections are used besides their positions to obtain the size of the unit cell.

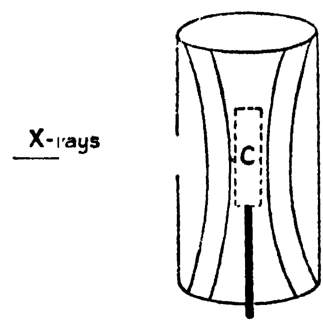


Fig. 94.—X-ray Powder spectroscopy.

127. The Rotating Crystal Method.—This was devised by Rinne, Schiebold, and Pôlányi, and has been used extensively in determining crystal structure. A monochromatic beam of *X*-rays, suitably defined by slit arrangements, falls on a crystal which is rotated about an axis perpendicular to the beam. The reflections are recorded on a circular film, as in the powder method. In some work, the crystal is rotated only through a small arc, in other experiments the crystal may be rotated through 360°. It is best to use a single crystal, as perfect as possible, but very small specimens may be employed. Good photographs are obtained by this method, but the work involved in deciding the structure from a study of the photographs is considerable. A typical rotation photograph is shown in Plate IV.

128. X-ray Grating Spectrographs.—It has been mentioned in § 125 that a crystal could be used as a diffraction grating for *X*-rays, and that when the lattice spacing of the crystal was known the wavelength of the *X*-rays could be deduced. Until quite recently this was the only method available for the determination of the wavelength of *X*-rays. The ordinary line grating, as used for ordinary light, could not be employed for *X*-rays owing to the very small wavelength. In 1930, Thibaud and Siegbahn devised spectrographs which used ruled gratings. It was not possible to rule gratings very

much closer than those used in work with ordinary light, but this was compensated for by making the rays to be analysed strike the surface of the grating almost tangentially. With a very small angle of incidence, it is possible to diffract ordinary X-rays with an appreciable angle, even if the grating has only 50 lines per millimetre. The results obtained with this apparatus agree with those using the crystal grating, and thus provide valuable confirmation of the earlier work.

129. Results of X-ray Analysis.—X-ray analysis of crystals has contributed largely to our knowledge of the crystalline state. In fact, we can say that we know more about the solid state than we do of the liquid state. The most striking result that has been achieved by its aid is the establishment of the fact stated at the beginning of this chapter, and which gives this chapter its title—the crystalline state—instead of the solid state. Almost all solid substances have been shown to be crystalline, and a definite arrangement of atoms has been shown even in certain liquids. Precipitates and colloids, previously thought of as amorphous, have been shown in the great majority of cases to be crystalline. The glasses, which were previously regarded as definite solids, are now thought to be supercooled liquids, and should not be treated as solids at all.

As previously mentioned, another great change in our idea of the solid state has been brought about by X-ray analysis, for it is clear that the term " molecule " now has no significance when we refer to solid salts.

X-ray analysis has also helped to elucidate the structure of organic compounds, by indicating exactly what the molecule is like and the nature of the linkages between the atoms. From a study of the crystal structures of aliphatic compounds, it has been shown that there is a tetrahedral arrangement of bonds about a carbon atom, the latter being united to four other atoms. The diamond has been shown to possess a structure in which each carbon atom is surrounded by four others, equidistant from it. This reminds one of the van't Hoff tetrahedral carbon model. The six-membered ring is also found in the diamond and graphite lattices. A study of hexa-methylbenzene and of naphthalene and anthracene shows the planar nature of the six-membered ring.

The difference in hardness between diamond and graphite also finds an explanation in the crystal structures which have been deduced for these two forms of carbon. Both have the hexagonal ring, but in the diamond there is a branching, which brings the planes of atoms closer together than in graphite. The two structures are shown in Fig. 95.

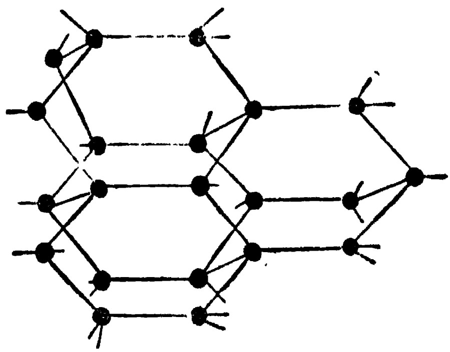
The distance between two adjacent planes in the diamond is

1·54 Å, whilst in graphite the distance is 3·25 Å. The increased distance in graphite makes it probable that the planes can slip more easily over each other than in diamond, and graphite is therefore soft, whereas diamond is hard.

The application of X-ray analysis to problems of stereochemistry has yet to be made.

X-ray analysis is providing a new method for investigating metals,

(a) Diamond



(b) Graphite

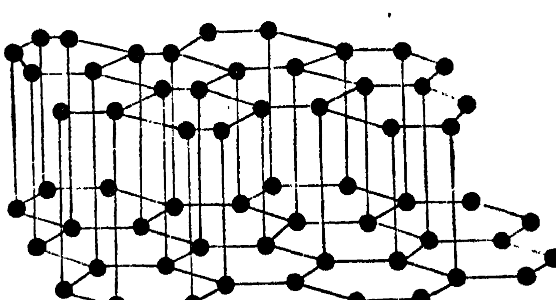


Fig. 95.—Structure of Diamond and Graphite.
[Based on diagrams in Tutton's *Crystalline Form and Chemical Constitution* (Macmillan).]

and the effects which take place on rolling, drawing, and heat-treatment. This work is of special value to the metallurgist. An X-ray study of steel and iron shows that when carbon is introduced into iron the large crystals of iron are broken up into a large number of small ones which interlace, and thus give to steel its strength.

Technical substances such as cellulose and rubber have been studied by this method. Cellulose has been found to possess a definite structure.

Vegetable and animal fibres, in general, give rise to X-ray diffraction patterns when a fine beam of X-rays is passed through a bundle,

about 1 mm. thick, of parallel fibres. These are usually called "fibre-photographs." A typical photograph for Ramie fibre is shown in Plate V.

The changes which take place when cotton is mercerised have been elucidated by the aid of X-ray analysis. Rubber has been found to crystallise and decrystallise as it is stretched and slackened (Hauser and Mark, 1926).

A mathematical treatment of the data obtained by X-ray diffraction experiments, in order to decide upon the space lattice of the crystal, has been used by J. M. Robertson in his work on the crystal structure of durene (1, 2, 4, 5-tetramethyl benzene), naphthalene and many other organic compounds. Since the crystal is essentially a periodic structure, the distribution of the scattering particles may be represented by a Fourier series. A Fourier analysis of the data reveals the detailed structure of the crystal and even the positions of the atoms in the molecules, the results confirming the conclusions of organic chemistry. For further information the student is referred to the original papers (*Proc. Roy. Soc.*, 1933, [A], **142**, 659–688).

130. Electron Diffraction in Crystals.– The fundamental point of wave mechanics (§ 56) is that moving electrons are associated with a wave-motion. As has been pointed out (in § 56) in 1924 de Broglie showed on purely theoretical grounds that this should be so, and stated that the wavelength λ of the motion would be given by $\lambda = h/mv$, where h is Planck's constant and mv the momentum of the particle. When this formula is applied to the case of moving electrons the wavelengths of the wave-motion associated with electrons which have fallen through potential differences of 10, 100, 1,000, and 10,000 volts, are found to be 3·86, 1·22, 0·386 and 0·122 Å respectively. If these wavelengths are compared with the wavelengths of X-rays, we find that they correspond roughly with very soft, soft, hard, and very hard X-rays. In 1925 Elsasser suggested that if de Broglie were correct, a beam of electrons should be diffracted at a crystal surface just as X-rays are. Davisson and Germer tested this with a plate of nickel. During the course of their work, their apparatus was, by accident, broken, and air entered On repeating the work, the reflexion from the nickel was found to have altered, and this was ascribed to a change in the crystalline state of the surface of the metal. They then experimented with a single crystal of nickel, allowing a beam of electrons to fall normally on the surface, and they found that the beam was not diffusely scattered, as the classical theory predicted, but that de Broglie's theory was true. A diffraction pattern was obtained which, if the wavelengths calculated by de Broglie were assigned to

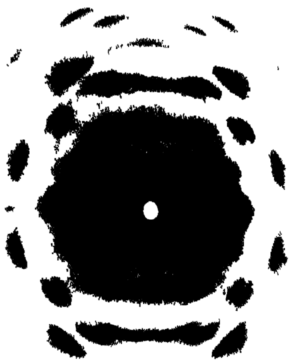


FIG. 1.—RAMIE.

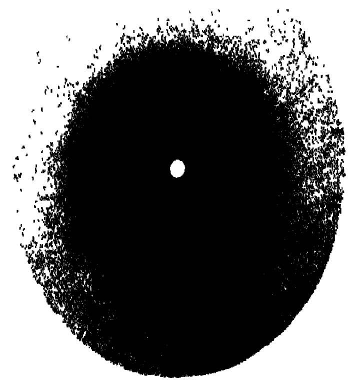


FIG. 2.—UNSTRETCHED RUBBER.

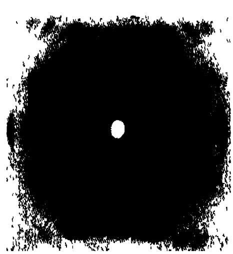


FIG. 3.—STRETCHED RUBBER.

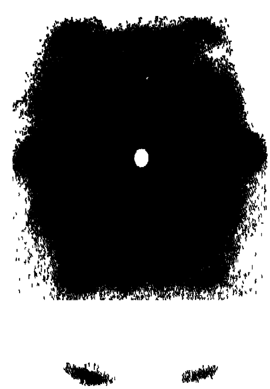


FIG. 4.—NATURAL SILK.

PLATE V.—X-RAY PHOTOGRAPHS OF RAMIE FIBRE, RUBBER, AND SILK.

Note that the photograph for Ramie is that of a typically crystalline substance. Natural silk is also crystalline. Unstretched rubber is not crystalline: it merely gives a ring, indicating its amorphous nature. On stretching, however, the rubber becomes crystalline, the photograph now showing a number of black spots, from the positions of which the crystalline form could be obtained.

(From Annual Reports on the Progress of Chemistry, 1931. Issued by the Chemical Society.

[To face p. 304.

[illegible]

the electron beams, obeyed Bragg's law. The work of many other observers in this field has also confirmed this.

It is obvious that this discovery provided another method of attacking the problem of the structure of crystals, and some very encouraging results have been obtained with it. Electrons have not the penetrating power of X-rays, and their action is confined to the first layer comprising a few tens of molecules. It is thus a very suitable method to employ for the investigation of thin films, where the X-rays scattered from these films could not be detected. G. P. Thomson has carried out a number of experiments in this direction. Pure copper does not give diffraction rings, but on exposure to air for a short time the rings due to cuprous oxide are produced. Similar oxide films were found on iron. The method has been applied to the study of "passivity." When a piece of iron is dipped into strong nitric acid, it becomes passive, and is unattacked by the acid, and on removal from the nitric acid it is unattacked by other reagents for some time. Two views have been held as to the reason for this. One states that an oxide film is produced, the other that an inert allotropic form of the element is formed. The former is the favoured view. If such a film were produced, it was thought that it should be indicated by this method of investigation, but it was found that no diffraction rings were produced. This is probably due to the fact that even a beam of electrons would not indicate a monomolecular film, such as the film of oxide may well be. It may, of course, not be crystalline at all, but amorphous, a view which is supported by the fact that the film of oxide which forms on aluminium when it is allowed to stand in air does not show any rings. The question is therefore left unsolved.

There is, however, a wide field available for this method of investigation, for our knowledge of thin films is very incomplete, and they are important in the study of metal corrosion, of plant and animal fibres, of fats on the surface of liquids, and of adsorbed gases. The fact that electron beams possess heating powers also makes this method useful for studying the changes in crystalline structure which take place at high temperatures.

The results of structure experiments carried out by the electron diffraction method agree closely with those obtained by the X-ray methods. The method has been applied for finding the structure of platinised asbestos. Platinisation probably results in a splitting of the fibres (D. A. Richards, *Phil. Mag.*, 1933, [vii.], **16**, 778–787). Davisson and Germer have investigated the structure of gold, tungsten, molybdenum and cobalt by this method, using electrons of high speeds. Their results agree with the ordinary X-ray observations.

131. **The Specific Heats of Solids.**—(a) *Elements.*—In dealing with the methods available for fixing the valency of an element when its equivalent is known, and thus determining its atomic weight, it was pointed out that Dulong and Petit, in 1819, put forward the law that the atomic weight of an element multiplied by its specific heat was equal to 6·4. It was also pointed out that the law was by no means of general application, and that it was necessary to use it with some precaution (p. 24). It is now possible to examine the reasons for the deviations from Dulong and Petit's Law.

Consider what happens when a crystal takes up heat at very low temperatures. When a crystal is heated the molecules in the crystal lattice carry out disordered oscillations about their mean positions in the lattice. Near the absolute zero these motions would be extremely small, and at the absolute zero they would cease altogether. Any small heat impacts that the crystal receives at this temperature will not be powerful enough to set the molecules in the interior of the lattice oscillating, since they are held by the very powerful crystal forces. Any interaction between the crystal and the heat impacts will be shown by the crystal as a whole. The whole crystal will vibrate when heat energy is absorbed at very low temperatures, and it will possess compressional and distortional vibration.

Debye and Tolman independently calculated the heat capacity of crystals in the neighbourhood of the absolute zero in its relationship with temperature by the aid of the theory of elasticity, and arrived at the result

$$C_v = k \times T^3,$$

where T is the absolute temperature and k is a constant. The equation was expressed somewhat differently by Debye

$$C_v = 71{\cdot}9 \times \frac{T^3}{\theta^3}.$$

Here the constant k has been split into two parts, and the equation refers to one gram-molecule of the substance. θ is a constant for any substance and has the dimensions of temperature. It varies from 50 for calcium to 1,840 for diamond.

Debye states that the equation holds up to $T = \theta/12$. The curve below shows the relationship between T^3 and C_v, and gives the observed and calculated values for carbon and aluminium. The falling off of the observed from the theoretical values is clearly shown. The curves agree at very low temperatures, but deviations occur as the temperature is increased.

Such deviations are due to the possibility of other types of oscillation. The Debye-Tolman equation was derived on the assumption that there was no movement of the molecules as indivi-

duals, but when this becomes appreciable it is not to be expected that the observed results will agree with the equation. The temperature at which such motion takes place will be dependent upon the crystal forces If these are weak, energy will be absorbed in producing oscillation of individual molecules at low temperatures. Weakness of crystalline forces is shown qualitatively by the ease of compression of a substance. A metal like lead, which is soft and easily compressed, has weak crystalline forces, so that this metal would show deviations from the above equation at low temperatures. Also, the lead molecules or atoms are heavy, and a considerable amount of energy will be absorbed in setting them into motion, so

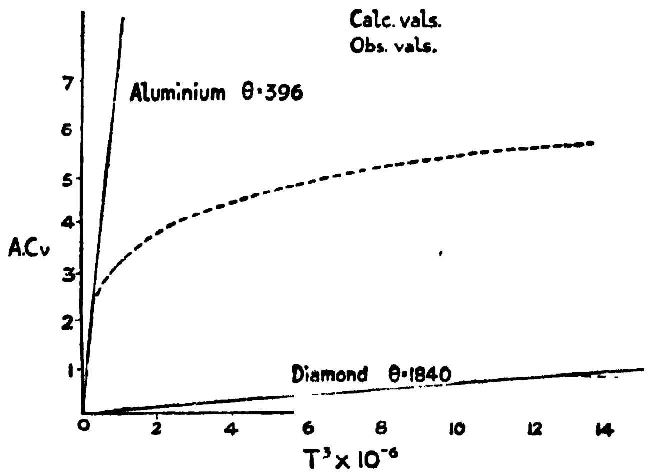


FIG. 96.—Relationship between Atomic Heat and Temperature for Aluminium and Diamond.

that large deviations are to be expected. With other crystals, however, such as the diamond, which is very hard, the crystal forces are great, and the Debye-Tolman equation holds up to comparatively high temperatures.

As the temperature is still further increased, the energy absorbed by a crystal will be taken almost entirely in producing motion of the individual molecules. In the end this motion becomes so great, and the crystal forces, in comparison, so small, that the crystal melts, and then probably loses its crystalline identity entirely. As the crystal approaches this state the average kinetic energy of the molecules will approach that of unrestrained molecules. For a monatomic substance this is known to be

$$\text{K.E.} = \frac{3}{2}RT \text{ gm.-cal. per gram-molecule (p. 192).}$$

Besides this kinetic energy, an oscillating body possesses potential energy, which can be shown to be equal to the kinetic energy. The total energy per gram-molecule is therefore,

$$E = 3RT = 6T \text{ gm.-cals. per gram-molecule.}$$

Hence the specific heat of a solid will approach 6 gm.-cals. per gram-molecule.

Many solid elements have reached the state just described at room temperatures, and consequently the atomic weight multiplied by the specific heat is a constant. Actually it comes out to be about 6·4. This is partly explained by the fact that the specific heat determined is at constant pressure, and will be slightly greater than that at constant volume. There are, however, some elements, notably carbon and boron, which have not reached the above condition, and therefore their atomic heats are considerably below 6·4.

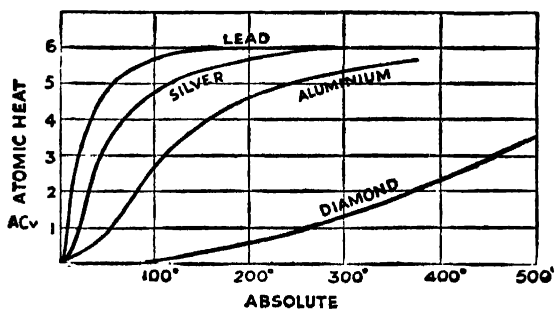


Fig. 97.—Curve showing variation of atomic heat at constant volume with absolute temperature for lead, silver, aluminium and diamond.

The explanation of the reason why Dulong and Petit's Law is a limiting law, and holds only when substances have reached a particular state, is now quite clear. It is obvious that it would be much better to multiply the atomic weight by the specific heat at comparable temperatures, instead of taking room temperature as standard.

The curves in Fig. 97 show the variation of atomic heat with temperature over an extended temperature range, and from this diagram it is clear that all substances would approach the value 6·4 for the atomic heat (at constant pressure ; the values plotted are at constant volume) as the temperature is increased.

(*b*) *Compounds.*—The molecular heat of a compound is approximately equal to the sum of the atomic heats of its constituents, *i.e.*, the specific heat multiplied by the molecular weight is equal to this sum. This is known as Kopp's rule.

It is clear that for most inorganic compounds the atomic heats of the constituents are far from 6·4. This value can be taken as correct for most metals, but for non-metals like sulphur and oxygen it is far from correct. The values that have been determined for these substances must be used. Thus, oxygen has an atomic heat of 4 cals., and sulphur 5·4 cals.

To calculate the molecular heat of zinc sulphate, we have

$$MC_p = 6{\cdot}4 + 5{\cdot}4 + 16 = 27{\cdot}8.$$

The specific heat of zinc sulphate is 0·174 cal. Hence the experimental value for the molecular heat is 161 × 0·174 = 28·01, which is in satisfactory agreement with the calculated value.

The specific heat of a compound can be calculated in a similar way if its molecular weight is known.

A better method of proceeding is to find the molecular heats for the acid groups from the specific heats of certain compounds, and then to calculate the molecular heat, or specific heat, of other compounds from these values.

132. Polymorphism.—Many solid substances exist in more than one modification. In fact, it is now correct to say that this is a general phenomenon, as it is known that the great majority of substances exist in more than one form. This phenomenon is called "polymorphism," although it is customary in the case of elements to use the term "allotropism," or "allotropy." There is no essential difference between these two terms, though "polymorphism" does not cover the allotropy of non-crystalline substances, such as oxygen and ozone, ortho- and para-hydrogen, active and ordinary nitrogen, and others.

Polymorphism is due primarily to differences in crystal structure, giving rise to differences in physical properties, such as density. If a substance will crystallise in more than one crystalline form, the two forms are polymorphs. Thus a substance may crystallise in the cubic system, in one form, whilst it may also crystallise in the triclinic system, thus providing a new form. Mercuric iodide is an example. When mercuric iodide is first precipitated it is yellow, but immediately changes to red. If the red form is heated to 126° C., it changes into the yellow form, which on cooling reverts to the red form. The latter crystallises in the tetragonal system as octahedra, whilst the yellow form crystallises in the orthorhombic system as plates. Salts such as cupri-mercuric iodide show the effect even better. This salt changes from red to black on heating to about 70° C., the reverse change taking place on cooling. Silver mercuric iodide changes from a buff colour to yellow at about 40° C., and changes back on cooling.

133. Energy Content of Polymorphs.—Since polymorphism owes its existence to differences in crystal structure, or to differences in the number of atoms which go to make up a molecule, it is clear that the polymorphs will have differing energy contents. The amount of energy contained by a substance will clearly be dependent upon the positions of the molecules in the space lattice. and their relative motion will be dependent upon the crystal forces. According to the second law of thermodynamics (§ 315), no change can take place spontaneously unless it is accompanied by a decrease in the free energy of the system. Consider again the case of mercuric iodide. The transformation of the yellow form into the red which takes place spontaneously is a typical example of such a process. The second law, then, states that this change cannot take place unless there is a decrease in the free energy of the system. It follows that the less stable form has the greater energy, and the more stable form is produced from it with loss of energy. When the unstable yellow form of mercuric iodide is transformed into the stable red form, energy is given out in the form of heat, and this energy must be supplied (by means of a Bunsen burner, or some other source of heat) if it is desired to convert the red form back into the yellow.

This, then, is a special case of a general theorem. Any spontaneous change is accompanied by a decrease in the free energy of the system. Certain cases of allotropic change are examples of spontaneous changes.

The fact that the energy of the stable form is less than that of the unstable form gives rise to differences in the vapour pressure of the forms. Vapour pressure is dependent upon the escape of molecules from the crystal lattice. When the molecules possess sufficient energy to vibrate in the lattice violently enough, they escape from the lattice, forming vapour. The vapour pressure of a solid is therefore some indication of the energy possessed by the molecules. It would be expected that the more stable form possessing less energy, and the molecules being therefore unable to vibrate with as great violence, would possess the lower vapour pressure, and the less stable form the higher vapour pressure. This is found to be true.

It would also be expected that the form possessing less energy, *viz.*, the stable form, would be less reactive chemically, and this is usually so.

The differences in vapour pressure of various forms of the same substance give considerable information as to the stability of the forms.

It was mentioned above that there was a spontaneous transformation of the less stable, or labile, form into the more stable form. This does not always start itself, but requires some sort of a

send-off. Many such examples are known. Thus, mercuric iodide may be kept for some time in the yellow form without returning to the red, but when it is touched by a rod, or scratched, it changes at once. Sulphur may be kept in the monoclinic form for some time, but if it is rubbed, the change to rhombic takes place rapidly. Substances which are in the labile state when the surrounding conditions are such that they would ordinarily be in the stable state, are said to be in the metastable condition. This term has been used before, concerning liquefied gases, and supercooling (p. 219). Many substances are capable of remaining in the metastable condition for a very considerable period, and particularly is this true of metals. In an English winter the ordinary form of tin is usually metastable. There are three forms of this metal, two of them being white tin and grey tin. The former is stable above 18° C., and the latter below this temperature. Hence, whenever the temperature falls below 18° C., as it frequently does in winter time, tin in its usual form is metastable. Tin articles have been known to change to grey tin in severe winters. Grey tin has a considerably smaller density than that of white tin (5·7 and 7·28 respectively), so that the change is accompanied by expansion, and the article usually falls to a powder. Such a change is commonly referred to as tin plague. It is related that when Napoleon marched his men out of Russia in 1812 the temperature was so low that the change from white to grey tin took place fairly easily, and the tin buttons and medals of the soldiers crumbled away.

As the temperature in this country is quite frequently below the temperature at which the one form of tin changes into the other, tin often becomes metastable and remains in the white form, although it should be converted into grey tin. If this change did occur, tin would be almost useless as a metal.

The temperature at which two forms of a substance become equally stable is called the transition temperature. It is the

TABLE LVI

Substance.	Form.	Transition Point, °C.
Sulphur	Rhombic $\rightleftharpoons$ Monoclinic	95·6°
Tin .	Grey $\rightleftharpoons$ White	13° ? 18°
	White $\rightleftharpoons$ Rhombic	202·8°
Zinc	$\alpha \rightleftharpoons \beta$	174°
	$\beta \rightleftharpoons \gamma$	322·0°
Ammonium chloride	$\alpha \rightleftharpoons \beta$	184·5°
Mercuric iodide .	Tetragonal $\rightleftharpoons$ Orthorhombic	126°
Silver iodide .	Hexagonal $\rightleftharpoons$ Regular	146·5°
Silver nitrate .	Rhombic $\rightleftharpoons$ Rhombohedral	160°

temperature at which both forms possess the same vapour pressure, and the same solubility, and may obviously be obtained by finding the point of intersection of the vapour pressure, or solubility curves. At a temperature slightly below this, one form becomes metastable and passes into the other, whilst at a temperature slightly above it the reverse change takes place. The transition point of the two forms of tin referred to above is 18° C., whilst that of the two forms of mercuric iodide is 126° C.

A table showing the transition points of various systems is given on page 311.

134. Types of Allotropy.—The distinction between various types of allotropy rests upon differences in the way in which the transition of one form to the other can be brought about.

In the first place, there are substances, the two (or more) forms of which are converted into each other at a definite temperature, the transition point. Examples of this type have already been given (mercuric iodide, tin, p. 311). When the substance is heated it changes from form A into form B, and the reverse change takes place on cooling. This is an example of a reversible transformation, and this type is called *enantiotropy*. It is well illustrated by the examples already given, to which may be added sulphur, the details of which are given in the table and in § 135.

Secondly, transformations are known which proceed at all temperatures in one direction. There is no definite transition point. The transformation of ozone into oxygen is a good example of this class. This is called *monotropy*, and is a case of irreversibility. Thus ozone breaks down into oxygen at all temperatures, but a reversal of the process by which the change was started does not lead to the re-formation of the ozone.

Thirdly, two allotropes may exist together in equilibrium. One form may be changing into the other at exactly the same rate as the reverse process is taking place. This is called *dynamic allotropy*, and is exemplified by liquid sulphur, which consists of a mixture of two forms of sulphur, designated as $S\lambda$ and $S\mu$, which are in equilibrium with each other, the proportions of each present being determined by the temperature.

135. Study of a System of each Type.—(*a*) *Enantiotropy.*—As already stated, a good example of this is the change of rhombic into monoclinic sulphur. If the vapour pressure of the rhombic form of sulphur is determined at various temperatures, the curve AB (Fig. 98) is obtained. There is, however, an abrupt change in the course of this curve at B, the temperature here being 95·6° C., and this is due to the change of the sulphur from the rhombic into the monoclinic form. In accordance with expectations, the vapour pressure of this

form is greater than that of the rhombic. At higher temperatures still, in the neighbourhood of 120° C., there is another abrupt change in the vapour pressure curve, and at this point the monoclinic form is converted into liquid. If the curve is continued it represents the vapour pressure of liquid sulphur, and ultimately a point will be reached at which the liquid boils, *i.e.*, the vapour pressure becomes equal to the superimposed atmospheric pressure. Here the curve comes to an abrupt end.

If now the conditions are reversed, and liquid sulphur is cooled from its boiling point, the vapour pressure follows the curve DC. It is possible to make the vapour pressure continue along the curve to E, without suffering any abrupt change at C. This happens when the liquid is supercooled, and no solid separates out. If, however, supercooling is prevented, there is an abrupt change in the direction of the vapour pressure curve at C, and the monoclinic form is produced—this being the stable form at this temperature. As this is cooled the curve CB is followed, and as in the case of liquid sulphur it is possible to supercool this form somewhat, no rhombic sulphur being formed. If this is so the curve BF is followed. If not the curve BA is retraced.

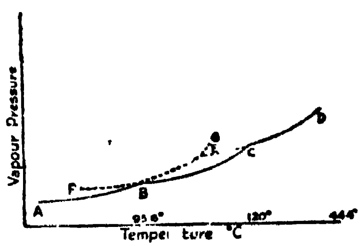


FIG. 98.—Vapour Pressure Curve of sulphur (enantiotropic System).

Obviously this is an enantiotropic system, for the changes are completely reversible, and there are definite transition points.

Enantiotropic changes are also characterised by the fact that the transition points of the solid forms lie below their melting points. The melting point of the rhombic form will be given by the point of intersection of the vapour pressure curves of the rhombic form and the liquid form; it is shown on the curve as the point E. The transition point of rhombic and monoclinic sulphur, *i.e.*, B, lies below the melting point of the rhombic form G and that of the monoclinic form C.

(*b*) *Monotropy.*—Another class of substances exhibiting polymorphism is that in which the change from one crystalline form to the other is not reversible. It is possible to pass only in one direction. The reason for this is that the melting point lies below the transition temperature of the two crystalline forms. Examples of this type of polymorphism are furnished by the compounds iodine chloride, ICl, and benzophenone. Each of the crystalline forms of these substances has its own melting point, those of iodine monochloride

being 13·9° C. and 27·2° C. and those of benzophenone 26° C. and 48° C. In each case the transition point lies above the melting point.

If a vapour pressure–temperature diagram is drawn to represent this type of system a graph of the form shown in Fig. 99 is obtained.

The curve AP_2 is the vapour pressure curve of the stable form, II, of the substance. At the temperature represented by P_2 the substance melts and passes into the liquid state, of which the vapour pressure curve is P_2B. The corresponding vapour pressure curve for the metastable form is CP_1. This form melts at P_1, and the curve P_1B is the vapour pressure curve of the liquid. The actual transition point of the two crystalline forms would be P_3, the point of intersection of the vapour pressure curves of the two forms, but as this is above the melting point of both forms it is never reached.

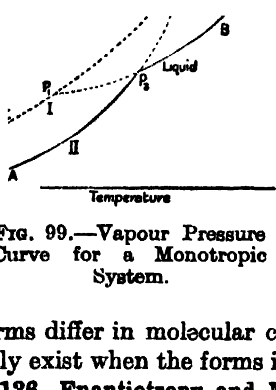


Fig. 99.—Vapour Pressure Curve for a Monotropic System.

(c) *Dynamic Allotropy.* — Certain allotropic forms of elements are capable of existing together in a state of equilibrium. There is no question of a transition point. The proportion of any one form present at equilibrium is dependent upon the temperature, and sometimes upon the pressure.

The best-known example of this is the allotropy of the two liquid forms of sulphur, $S\lambda$ and $S\mu$, which coexist in ordinary molten sulphur. These forms differ in molecular complexity. This type of allotropy can only exist when the forms involved are miscible, or partly so.

136. Enantiotropy and Monotropy Combined.—It is possible for the two types of allotropy—enantiotropy and monotropy—to exist in the same system, if the substance concerned can exist in more than two crystalline forms. Sulphur is a case in point. It can exist in eight different crystalline forms, but of these the only two which show the relationship of enantiotropy towards each other are the rhombic and monoclinic forms. All the other forms are metastable with respect to rhombic and monoclinic sulphur, even up to the melting point, *i.e.*, their transition points lie above the melting point, and they are therefore monotropic.

137. Methods of determining Transition Points.—There are several methods by which transition points may be determined, though in any particular case it is usually found that one presents many advantages over another. Besides their use for investigating the transition of one allotropic form into another, many of these methods

are applicable to the study of equilibrium between salt hydrates (see p. 395). The first method is the :—

Thermometric Method.—It may be regarded as a general rule that, when one phase changes into another, heat is either absorbed or liberated. Thus, if water is gradually heated, its temperature slowly rises until the boiling point is reached, when it remains stationary until all the water has boiled away. This is due to the fact that heat is taken up in causing the change of state—the latent heat of evaporation. Similarly, if water is cooled, its temperature gradually decreases until the water starts to freeze, when it remains constant. When all the water is converted into ice the temperature again falls.

The same considerations affect the change of phase which takes

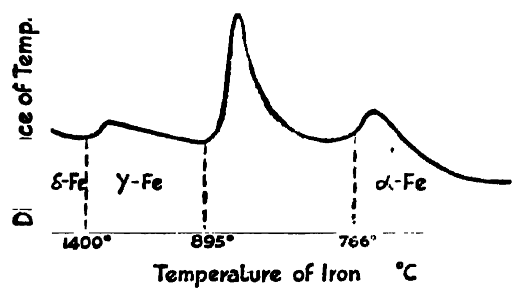


FIG. 100.—Cooling Curve for Iron.

place at the transition point. If a substance is cooled from above the transition point, when the transition point is reached the temperature remains constant, or may actually appear to increase a little if any considerable supercooling takes place. This is well shown by the figures obtained in the cooling of iron. If iron is cooled from its melting point and the difference in temperature between a platinum wire cooling with it, and the iron itself, is noted at different temperatures, and the results are plotted, a curve is obtained similar to that shown in Fig. 100.

As one form of iron changes into another, there is an evolution of heat, causing the ascents in the curve. From the melting point down to 1,400° C. a form of iron known as δ-iron is stable. Little is known about it. From 1,400° C. to 895° C., γ-iron is the stable form. Where the δ-form changes over to the γ-form there is an evolution of heat, not very large, but sufficient to cause a slight hump in the curve. γ-iron is the form in which iron usually crystallises from its alloys. It has the power of forming solid solutions

with carbon. At 895° C. γ-iron changes into α-iron, and here there is quite a large evolution of heat. This was the first of these transition points to be discovered, for the amount of heat evolved is much greater than at the other transitions. If a piece of iron heated to 1,000° C. is allowed to cool, the amount of heat given out at this temperature is sufficient to cause the iron to glow, and hence the phenomenon has been termed *recalescence*. γ-iron has no magnetic properties. At 766° C. the α-form becomes magnetic. α-iron is the principal constituent of wrought iron.

Dilatometric Method.—When one allotropic form changes into another there is usually a change in volume. To determine the transition point it is necessary to determine the temperature at which this change in volume occurs. This can be done by means of the dilatometer, an instrument somewhat like a thermometer in design, but having a larger bulb. Originally, the instrument is made of the form shown in Fig. 101, i. The bulb A has not yet been sealed off. It is connected to a capillary tube, backed by a scale. The substance to be examined is introduced into the bulb A through the tube B, which is then sealed off. A liquid which does not act chemically on the substance to be examined is introduced into the tube, so that it covers the solid, and reaches a level on the scale. The apparatus is now gradually warmed in a bath, of which the temperature is noted. At each reading of the temperature, the height of the liquid in the tube is noted. Up to a certain temperature (the transition point), the liquid will rise uniformly in the tube, as there is uniform expansion of liquid and solid, but at the transition point there will be an increase in volume of the solid due to change in its form, and hence an additional rise of the liquid in the tube. After this the expansion is once again uniform. On cooling, the reverse series of changes takes place.

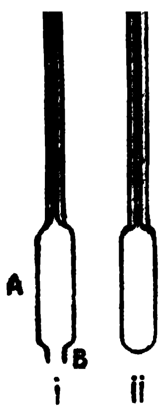


FIG. 101.—Dilatometer. (i.) unsealed, (ii.) sealed.

Usually there is a certain lag in the expansion or contraction, and the curves obtained for the two cases are shown in Fig. 102. The curve ABCD is the heating curve; the curve DCEF is the cooling curve. If there were no lag, the portions of the curve indicating a rapid increase in volume would coincide. It is obvious that they do not. The correct transition point is the mean of the temperatures indicated by the two processes.

Another method of using the dilatometer is to fill the bulb with a

mixture of the two forms, the transition point of which is to be determined. If the instrument is now placed in a bath, the temperature of which is exactly the transition point of the two forms, they will not be altered in any way, and consequently there will be no change in volume. If an expansion is found, the temperature of the bath is altered until there is a slight contraction. The transition point lies between these two temperatures, and can be determined by careful adjustment of the temperature of the bath. The method was used by Reicher (1884), to determine the transition point of rhombic and monoclinic sulphur. A mixture of the two forms was placed in the bulb, and a mixture of 1 part of carbon disulphide and

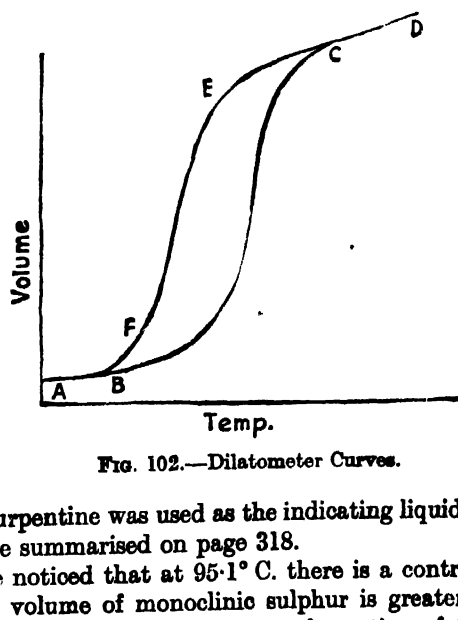


FIG. 102.—Dilatometer Curves.

5 parts of turpentine was used as the indicating liquid. The results obtained are summarised on page 318.

It will be noticed that at 95·1° C. there is a contraction. Since the specific volume of monoclinic sulphur is greater than that of rhombic sulphur, this signifies a transformation of the monoclinic into the rhombic form. At 96·1° C. there is an expansion, showing that the reverse change is taking place. At 95·6° C. there was practically no change. The dilatometer in this experiment was sealed up, and the pressure developed was about 4 atmospheres. The value of the transition point obtained must be corrected if the value at atmospheric pressure is required.

Measurement of Vapour Pressure.—It has already been noted that the vapour pressures of allotropic forms are different, but it is obvious that at the transition point they become the same. If, then, the temperature at which the vapour pressures of two allo-

TABLE LVII[1]

Temperature, 95·1° C.

Time, mins.	Level of Liquid, mm.
5	343·5
30	340·5
55	335·75
65	333

Temperature, 95·6° C.

Time, mins.	Level of Liquid, mm.
5	368·75
100	368
110	368·75

Temperature, 96·1° C.

Time, mins.	Level of Liquid, mm.
5	342·75
30	354·75
55	360·5
60	361·5

tropic forms become identical can be determined, it gives the transition point. The simplest method of determining the vapour pressure of a solid is by means of a tensimeter. One form of the apparatus (illustrated in Fig. 103) consists of two bulb tubes connected to the limbs of a U-tube. The U-tube is filled with some manometric liquid such as pump oil. If it is desired to find the vapour pressure of a salt hydrate, some of the hydrate is placed in the bulb *d*, and strong sulphuric acid in *e*. The necks *d'* and *e'* are then sealed off. The instrument is now placed on its side so that the liquid in the U-tube runs into the bulbs *a* and *b*, and it is exhausted by a pump connected at *f*. After complete exhaustion, the neck is sealed at *f*. The apparatus is now set up vertically in a

[1] This table is taken from A. Findlay, *The Phase Rule* (Longmans), 1923, p. 284. The student is referred to this book for further details of the determination of transition points.

thermostat, and the differences in the levels of liquid in the U-tube noted. The vapour pressure of the sulphuric acid may be taken as zero, hence the difference indicated is a measure of the vapour pressure of the salt hydrate. Observations are made at various temperatures.

When dealing with allotropes, one form may be placed in one

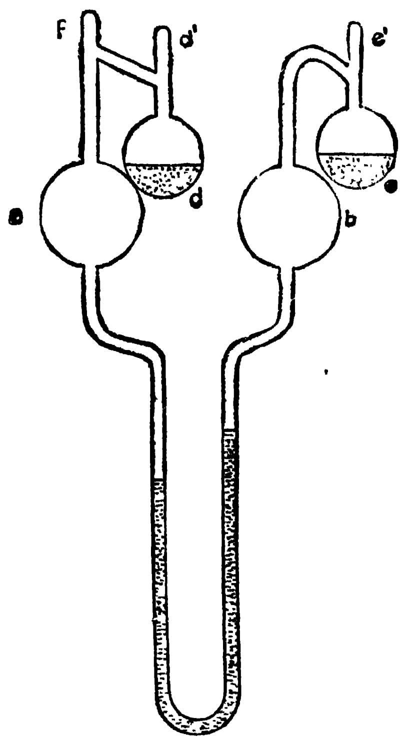


FIG. 103 —Tensimeter.

bulb and one in the other. Both bulbs are heated to the same temperatures, and when their vapour pressures become equal there will be no difference in level in the U-tube. At this temperature both substances are equally stable, *i.e.*, the temperature is the transition temperature.

All the usual methods for determining vapour pressure can be used also for these measurements, but the one described is the most convenient.

Change in Solubility.—At the transition point, the solubility of the two forms becomes the same. The method is, however, usually

employed for determining transition points between salt hydrates. Thus, if the solubility of ordinary crystalline sodium sulphate is plotted, it is found that there is a distinct break at 32·383° C. At this temperature sodium sulphate decahydrate, $Na_2SO_4.10H_2O$, is converted into the anhydrous salt, which has a solubility curve altogether different from that of the hydrate. The temperature at which the break occurs is the transition point between these two forms (Fig. 104).

Ammonium nitrate exists in five different crystalline forms. In each case there is a different solubility curve. The form known as β-rhombic passes into γ-rhombic at a temperature of about 32° C., and so there is a break in the solubility curve at that point (Fig. 105).

It will be realised that the point where the break occurs is really the point of intersection of two separate solubility curves, and at that point both forms have the same solubility.

Optical Methods.—Sometimes there is a visible alteration in one form when it changes into another. Thus the colour changes of the mercuric iodide complex salts, and of mercuric iodide itself, can readily be observed, and the temperature at which the change takes place is the transition point. Changes in crystalline form, when unaccompanied by changes in colour, may be observed under the microscope. Also, changes in the refraction of crystals can be thus observed.

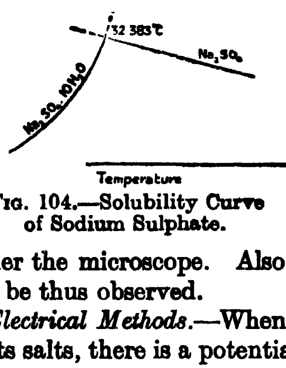


FIG. 104.—Solubility Curve of Sodium Sulphate.

Electrical Methods.—When a metal is placed in a solution of one of its salts, there is a potential difference between the metal and the solution. The amount of this potential difference depends upon the form of the metal, and the concentration of the solution. If, therefore, an electrical cell is made up of a metal, say tin, with one electrode of one allotrope and the other of the other allotrope, placed in a solution of a salt of the metal, say ammonium stanni-chloride, the cell will possess a certain electromotive force (E.M.F.), which could send a current through an external circuit. If arrangements are made to warm the cell, when the transition point is reached, the two forms become equally stable and have the same potential with respect to the solution. Hence, at this temperature the cell has no E.M.F. It is thus possible to determine the transition point with accuracy. The method will be more fully understood after reading Chapter XVI.

Other Methods.—The transition temperatures of some salts have been found by plotting the viscosities of saturated solutions at

various temperatures. A sharp break in the viscosity curve occurs at the transition point.

An interesting method that has been used to determine the transition point between α- and β-zinc is the resistance to indentation.

Conductivity for heat and electricity has also been used for this purpose. Indeed, it may be said that almost any physical property can be used for determining transition points, for the physical properties of allotropes or polymorphs usually differ considerably.

138. Comparison of Melting Points and Transition Points.—(1) *Analogies.*—(*a*) Both transition temperatures and melting points are perfectly definite temperatures, and may be used for thermometric standards. It is usual to employ the melting point of ice as a fixed point in thermometry, but transition points are equally suitable and have frequently been proposed as subsidiary standards. Many transition points are known correct to one-thousandth of a degree. Thus, the transition point of sodium sulphate decahydrate to the anhydrous salt is known to be 32·383° C., and has been proposed as a fixed point in thermometry.

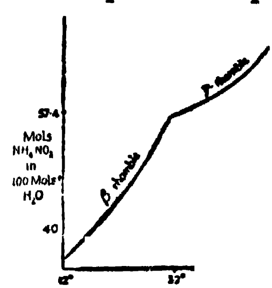


FIG. 105.—Solubility curve of ammonium nitrate.

(*b*) Both transition points and melting points are affected by pressure. The way in which the transition point is altered depends, like the case of the melting point, on whether the new phase occupies a larger or smaller volume than the old. Some substances expand on transition. In this case the transition point is raised by increase of pressure. If contraction occurs on transition, increase of pressure causes a lowering of the transition point. This is an application of the theorem of Le Chatelier and Braun [1] that whenever a constraint is placed on a system in equilibrium, the equilibrium is altered in such a way as to tend to annul the effect of the constraint. The effect of an increase in pressure on a body is to decrease its volume. Consider two forms of a substance, A and B, the form A being stable above the transition point, and B below it. Suppose the two forms are existing together in equilibrium at the transition point. When the extra pressure is applied, the result is to transform the substance entirely into that form which has the smaller volume, thus tending to annul the effect of the pressure. In other words, the equilibrium

[1] This theorem is sometimes referred to simply as the theorem of Le Chatelier, and sometimes as the theorem of Le Chatelier and Van't Hoff.

condition is entirely upset, and in order to restore it the temperature must be raised or lowered. Thus, the new transition point will be either above or below the old, according to which form has the less volume.

(c) At both transition point and melting point there is an evolution or absorption of heat when passing from one phase to the other. The stable form at higher temperature always passes into that stable at lower temperature with heat evolution, a fact made use of in the determination of transition points by the thermometric method already referred to. The same applies to melting points. The reverse effect is found in the transition from a form stable at low temperatures to that stable at high temperatures. Here there is an absorption of heat. Both these effects follow from Le Chatelier's theorem. At the transition point both forms are equally stable. If the mixture of the two forms at the transition point is heated, the equilibrium will be shifted in such a way that heat is absorbed. Hence the form stable at high temperatures must be formed with absorption of heat. On the other hand, if the mixture of two forms at the transition point is cooled, that form will be produced which is stable at low temperatures, and it will be formed with evolution of heat.

(d) The addition of a second substance causes the transition point to be lowered, just as it causes a depression of the freezing point.

(2) *Differences.*—(a) Transition points usually mark the change from one solid phase to another solid phase, whereas the melting point marks the transition from a solid to a liquid phase. The change in the case of transition will be considerably slower than with melting, for the movement of molecules in solids is slower than in liquids, and it will therefore take a longer time to rearrange the molecules.

(b) Arising out of this, it is clear that owing to the difficulty experienced by molecules of solids in changing their arrangement, it is quite possible to superheat a form without the transformation taking place. Thus it is possible to superheat rhombic sulphur and get no monoclinic sulphur formed. This is not possible with the melting point. It is almost impossible to superheat a solid above its melting point.

139. Study of some Common Allotropic Systems.—(1) *Sulphur.*—There are said to be more allotropes of sulphur than of any other element, but there is not the slightest doubt that many of the so-called "allotropes" are mixtures. The chief forms are :—

α-Sulphur (Rhombic or Octahedral).
β-Sulphur (Monoclinic or Prismatic).
Nacreous Sulphur.

Tabular Sulphur,
γ-Sulphur (Plastic),
δ-Sulphur (Amorphous),
Colloidal Sulphur,
λ-Sulphur,
μ-Sulphur,
π-Sulphur (possibly) } forms of liquid sulphur.

The allotropy may conveniently be considered under the headings :—

I. Solid equilibria, enantiotropic changes.
II. Crystalline solid monotropic forms.
III. Liquid sulphur.
IV. Colloidal systems.

I.—Ordinary α-sulphur is enantiomorphic with β-sulphur. When α-sulphur is heated to 95·6° C., it is converted into the β-form, and when the latter is cooled it reverts to the α-forms at this temperature—the transition point. The molecular formula of these two varieties is S_8. This formula has been obtained by studying the lowering of the freezing points of certain solvents, on dissolving known amounts of the forms in them. Study of the elevation of the boiling points of these solvents, when sulphur is dissolved in them, leads to the same result (§ 237).

II.—Nacreous, or mother of pearl sulphur, was discovered by Gernez in 1884. Molten sulphur, after heating in a test-tube to above 150° C., is cooled down to, and maintained, at a temperature of 100° C., in a water-bath. On gently scratching the walls of the tube with a glass rod, the sulphur crystallises in the nacreous form. It can also be obtained by crystallisation of a solution of sulphur in benzene, but special conditions must be observed. It is monoclinic, but has not the same interfacial angles as β-sulphur. This is an example of monotropy in the sulphur system, for nacreous sulphur is always metastable, changing to rhombic or monoclinic sulphur according as the temperature is below or above 95·6° C. It is, however, possible to melt nacreous sulphur at 106·8° C., before it has had time to change into another solid form.

Tabular sulphur is said to be formed when solutions of ammonium sulphide in alcohol are oxidised at temperatures below 14° C. It is also monoclinic, but with different angles from β-sulphur. Like nacreous sulphur, it is a monotropic form.

III.—Liquid sulphur presents a difficult problem. When sulphur is heated to a temperature above its melting point it forms, at first, an amber-coloured liquid, which, as the temperature is increased, becomes darker and more viscous, until, at one stage, it cannot be

poured from the tube. As the temperature is increased still further, the liquid becomes more mobile, until finally it boils. The changes in colour and other physical properties are due to the change in the relative proportions of two allotropes, known as λ-sulphur and μ-sulphur. Aten (1912–13) believed that another allotrope, π-sulphur, was also present in the liquid, but this conclusion is open to some doubt. It is now generally considered that liquid sulphur consists of the two allotropes, $S\lambda$ and $S\mu$, in dynamic equilibrium (Ch. VIII.). These two allotropes are not completely miscible, but form a sol (§ 329). The amber-coloured liquid formed when sulphur first melts seems to be pure $S\lambda$, but as the temperature is increased $S\mu$ is formed in increasing quantities, until, at the boiling point, the liquid is almost pure $S\mu$. $S\mu$ is probably colloidal, and has a high molecular weight. From the work of West and Menzies on the thermal data for liquid sulphur, high molecular weights are to be expected, possibly as high as S_{16}.

IV.—When liquid sulphur is rapidly cooled, plastic sulphur, or γ-sulphur, is produced. The nature of this form may vary, since it will depend upon the composition of the liquid from which it is prepared. It is a rubber-like mass, and may be a gel (§ 329), since sols (liquid sulphur is a sol) often give gels on solidifying. If this is so, the continuous phase is, probably, β-sulphur, and the disperse phase μ-sulphur. The structure of plastic sulphur has recently been studied by Trillat and Forestier, who find that this form is not amorphous, as would be the case if it were merely a supercooled liquid like glass. X-ray examination shows that the sulphur gives a "fibre photograph" (p. 304), with a definite crystalline form. This may be due to the β-sulphur. These observers noted also that exposure to X-rays caused a rapid conversion of plastic into rhombic sulphur.

Colloidal sulphur itself is frequently produced in chemical reactions involving sulphur compounds. Thus, when dilute hydrochloric or sulphuric acid is added to a dilute solution of sodium thiosulphate, a solution is obtained containing colloidal particles of sulphur. The colloidal sulphur may be coagulated by the addition of an electrolyte.

The nature of amorphous sulphur, δ-sulphur, has not yet been fully established. This substance has yet to be examined by the X-ray method, when possibly it may be found to be micro-crystalline. This form of sulphur is obtained by adding an acid to a solution of a polysulphide, such as yellow ammonium sulphide. The fact that it is soluble in carbon disulphide, like α- and β-sulphur, lends support to the view that it may be micro-crystalline.

(2) *Phosphorus.*—There are three real allotropes of phosphorus, which are named according to their colour, white, violet and black

phosphorus. Red phosphorus is a solution of violet in white, whilst the so-called "scarlet phosphorus" of Schenck is merely violet or red in a fine state of division.

White phosphorus, which is the form commonly occurring, is not the stable form. The system is monotropic (p. 312). There is no definite transition point between white and violet phosphorus, as the transition point lies above the melting point. When the liquid obtained from any form is cooled, it does not follow the stable curve, but passes across to the metastable, along P_2P_1 in Fig. 99. Thus white phosphorus is always formed as a result of cooling liquid phosphorus. This follows the "law of successive reactions" enunciated by Ostwald (§ 142).

White phosphorus is the metastable form, and that this is so is evident from many of its properties. It is by far the most reactive form. It therefore contains more energy than red or violet. More heat is given out in its combustion. It will glow. It has the greater vapour pressure at ordinary temperatures.

Violet phosphorus is obtained by crystallising phosphorus from molten lead or bismuth, and then dissolving away the metal electrolytically, or with nitric acid. This form has a much lower chemical activity than the white form. It does not glow, and it has a lower heat of combustion. It also has a lower vapour pressure at ordinary temperatures.

Red phosphorus is known to be a solid solution of white in violet, because of its varying properties. According to its mode of preparation, it contains varying amounts of white phosphorus, which can be removed by careful washing with water, when the violet form is left. It also varies in colour, though this may be due to variation in particle size rather than in composition of the solution.

The point to be emphasised about the allotropes of phosphorus is that they form a monotropic system, there being no transition point.

By exposing white phosphorus to great pressure at 200°, Bridgman prepared a black form of phosphorus. In properties this is similar to violet, but is a better conductor of heat and electricity.

White phosphorus appears to exist in two forms with a transition point at − 77° C. at amospheric pressure.

(3) *Carbon.*—There are probably only two allotropes of carbon—diamond and graphite. At one time it was customary to call each form of charcoal an allotrope of the element, but *X*-ray analysis shows that some of them are microcrystalline and have the graphite structure, and therefore should not be called separate allotropes. They are probably merely graphite in a very fine state of division. This may be true of all the charcoals—or so-called

"amorphous" forms—although all of them have not yet been examined.

Diamond and graphite differ in their crystalline structure, but as regards their stability there is very little difference. This accounts for the fact that transition from one form to the other is extraordinarily slow. The heat of combustion of diamond is 7,873 gm.-cals. per gram, whilst that of graphite is 7,832 gm.-cals. per gram. These figures indicate that the intrinsic energies (pp. **611**, **617**) of the two forms are almost identical, but that diamond, as it contains slightly more energy, is the metastable form at ordinary temperatures. However, the conversion of diamond into graphite has never been observed to take place spontaneously at any temperature.

(4) *Nitrogen.*—If the silent electric discharge is passed through nitrogen, a form of the gas with enhanced activity, called "active" nitrogen, is produced. This active nitrogen, as would be expected, is very unstable. It changes back to the ordinary form with the emission of light.

The chemical activity of the gas is shown by the fact that it combines directly with the vapours of many metals, giving nitrides. It reacts with sulphur at 100° C., giving a mixture of nitrogen sulphides. It also combines directly with phosphorus and with many types of hydrocarbons. With nitric oxide, a very peculiar reaction takes place :—

$$N_{active} + 2NO = NO_2 + N_2.$$

The nature of active nitrogen is still unknown. As the glow is increased by cooling, and decreased by heating, it was at first thought that the re-formation of nitrogen molecules was taking place by the combination of smaller units, such as atoms. Heat would tend to prevent this. If active nitrogen consisted of atoms of nitrogen, or of molecules with the formula N_3, it ought to be possible to liquefy the gas, but this has never been done. If, too, the gas consisted of single atoms, the amount of energy imparted by the discharge should be sufficient to cause the breakdown of the molecules to form these atoms, but calculation shows that it is quite insufficient for this task. It seems probable that energised molecules are produced by the electric discharge. Sir J. J. Thomson suggests that the outer ring of electrons, which in ordinary nitrogen contains five, may divide into four and one, thus giving a molecule with increased energy.

(5) *Hydrogen.*—Recently it has been shown that ordinary

hydrogen consists of two distinct forms which differ slightly in physical properties. Their existence was predicted from calculations based on wave-mechanics. Hydrogen was stated to be capable of existence in two forms differing in nuclear spin (p. 140). A short time later, hydrogen was actually separated into its two allotropes, by fractional adsorption on charcoal under pressure, at the temperature of liquid air. The two forms are called ortho- and para-hydrogen, and the ordinary gas is an equilibrium mixture containing about 67 per cent. of the ortho form. As an example of differences of properties of these two forms of hydrogen, melting points may be quoted : that of para-hydrogen is 13·83° Abs., that of ortho-hydrogen is 13·96° Abs. There is also a difference in boiling point, and in specific heat.

(6) *Tin.*—Tin is a trimorphous metal. The upper transition temperature is 202·8° C., and the lower 18° C., though some estimates have placed the latter at 13° C. Reference has already been made to the existence of two enantiomorphous forms of tin with the lower transition point, and it was pointed out that ordinary white tin is frequently in the metastable condition in this country. The change from white to grey tin is very sluggish, and if it were not for this tin would be practically useless as a metal. The reverse change from grey to white is not so slow, and takes place rapidly when hot water is poured over grey tin. The change from white to grey takes place much more readily when nuclei of grey tin are already present, and it therefore appears to spread by infection ; hence the name " tin plague " which has been given to this change.

The transition at the higher temperature is from tetragonal to rhombic crystals. Tetragonal tin has the highest density of the three forms.

$$\underset{\substack{\text{Sp. gr.}\\5{\cdot}80}}{\text{Grey tin}} \xrightleftharpoons{18^\circ\ \text{C.}} \underset{\substack{\text{Sp. gr.}\\7{\cdot}286}}{\text{Tetragonal tin}} \xrightleftharpoons{202{\cdot}8^\circ\ \text{C.}} \underset{\substack{\text{Sp. gr.}\\6{\cdot}56}}{\text{Rhombic tin}}$$

(7) *Antimony.*—Antimony exists in a number of allotropic modifications. Yellow, or α-antimony, is very unstable, and is formed by the action of ozonised oxygen on liquid stibine at $-90°$ C. It changes readily into a black powder, thought to be amorphous. This in turn soon changes into the ordinary form of antimony, the rhombohedral or β-form, at ordinary temperatures. Amorphous antimony was obtained by Gore in 1858 by the slow electrolysis of a strong solution of antimony trichloride in hydrochloric acid with a platinum cathode and an antimony anode. This form is very unstable, and when scratched falls to a powder with a slight

explosion. As the fumes given off in this explosion always contain antimony trichloride, it is thought that this so-called "allotrope" is only a solution of the trichloride in black amorphous antimony.

140. Velocity of Transformation of Metastable into Stable Forms.— It has already been mentioned that the change from one form to another does not necessarily take place rapidly. There are numerous external conditions which alter the speed at which the change takes place. Many transformations of metastable into stable forms take place with extraordinary slowness. In fact, in some cases the form of a substance ordinarily met with is the metastable form which has not changed, and shows no signs of changing, into the stable form. White phosphorus, for example, is metastable, and shows no inclination to change into red except in the light; and, as already stated, there are frequent occasions upon which white tin is metastable, and yet the sluggishness that characterises the change from white to grey tin makes it possible to preserve articles made of white tin indefinitely. Often the slowness is due to the fact that crystal forces of some magnitude have to be overcome, and bonds broken and re-made. Where the new phase has not appeared, the transformation is said to be "suspended."

It has been found that, in order to avoid suspended transformation, it is necessary to have present a small quantity of the phase it is desired to obtain. The effect of "inoculation" of a system with a crystal of the substance required from it is well known. The amount of substance required to act in this way is exceedingly small, and has been measured in the case of supercooled salol, 1×10^{-7} gms. being sufficient to bring about crystallisation. The presence of this small amount of substance provides a certain number of crystallisation nuclei, around which others form, and the whole mass crystallises.

Mechanical shock can also bring about transformation. Hence the value of stirring and scratching the sides of the vessel containing the melt in bringing about crystallisation. The mechanism of this method is not known.

It must be understood that it is not all solids that can bring about crystallisation from a system in suspended transformation. Only the substance itself, or one possessing a very similar crystal lattice, is effective.

The velocity of crystallisation of supercooled liquids has been studied by a number of investigators. The supercooled liquids were placed in narrow glass tubes, and crystallisation was started by inoculation. The time taken for the crystallisation to get a certain distance along the tube was determined. It was found that

for any given degree of supercooling the velocity of crystallisation was constant. As the degree of supercooling is increased, the velocity of crystallisation also increases up to a maximum. This maximum remains constant over a large range of temperature, after which it diminishes again, and for very severe supercooling may become zero. This is probably what has happened in the case of glass.

The velocity of transformation is affected in various ways by many other external agencies. Thus the addition of a liquid which dissolves both forms may considerably accelerate the velocity of transformation. At the transition point, the solubilities of the two forms become equal, but at any given temperature, the solubility of the more stable form is less than that of the less stable. If two solid phases are brought into contact with a solvent which dissolves both of them, it will dissolve one form more than the other. The solution will become saturated with respect to this form, the less stable one, but is then supersaturated towards the stable form, and this is deposited. An example of this is the well-known fact that tin changes more readily from white to grey in the presence of a solution of ammonium stanni-chloride. It is necessary to state, however, that a solvent may sometimes retard the velocity of transformation, especially if it be viscous.

Temperature may affect the change. As already mentioned, the velocity of crystallisation of a supercooled melt depends upon the temperature.

Certain substances, added in small quantities to the system, may cause the change to be brought about more readily, acting in this way as catalysts. The best-known case of this is the acceleration of the change of white phosphorus into red by the addition of a very small quantity of iodine.

141. Mechanical Strains in Metals.—The question of metastability of metals has received a good deal of attention because of its great practical bearing in everyday life. The practical usefulness of many metals depends alone upon their metastability.

When copper and some other metals are stretched and rolled and hammered, their properties are considerably altered. They become harder, and their tensile strength increases. This can be shown to be due to a change of state of the metal, the new state being metastable because the metal possesses a higher solution pressure after treatment than it did before, resulting in its being more electronegative with respect to a solution of one of its salts (§ 322).

It is thought that a metal in this metastable condition is very much like glass. In the process of working, the crystals are, in part, broken down, and the substance becomes semi-amorphous.

Just as glass devitrifies on heating, so the metal after treatment, when it is heated, passes from the semi-amorphous, metastable state into the crystalline stable state.

142. The Law of Successive Reactions.—It has frequently been observed that when a substance passes from a metastable into a more stable condition, it does not reach the most stable form at once, but attains it through successive stages. If sulphur vapour is cooled it is first transformed into a liquid, which solidifies in the monoclinic form and slowly changes to the rhombic. The liquid sulphur does not change at once into rhombic sulphur. White phosphorus is always formed when phosphorus vapour is cooled, although it is the metastable state, and only with extreme slowness is violet phosphorus formed from it. In organic chemistry it is frequently found that a substance is deposited as an oil, which gradually undergoes solidification to crystals. The oil is not the stable form, or it would not spontaneously crystallise.

There are a very large number of these examples, and Ostwald has made the generalisation called the *law of successive reactions* to embrace them. This states that when a system passes from a less stable condition it does not pass directly into the most stable, but reaches this by traversing intermediate conditions of progressively greater stability.

There are some apparent exceptions to Ostwald's Law, but it may be taken as true in the great majority of cases.

143. Smits' Theory of Allotropy.—It has already been stated that allotropy is thought to be due to change in crystalline form, though it has not been said why there should be such a change. Smits' theory of allotropy differs considerably from this. He regards solid bodies as complex mixtures of various molecular species. The molecules can be single, double, triple, and so on. All these molecular aggregates are in inner equilibrium. If this equilibrium is disturbed in any way, and cannot be restored, the properties of the substance will change, and we shall have an allotropic form. There is no doubt that solids are highly complex and made up of various molecular aggregates. Strictly speaking, it is not possible to talk about the molecular weight of a solid owing to the various degrees of polymerisation met with. Smits' theory has been very useful in solving some problems concerning the equilibrium relations of polymorphic substances, but has not been sufficiently investigated.

It has provided an explanation of the problem of intensive drying.

144. The Effect of Intensive Drying on the Properties of Liquids.—When a liquid is dried very completely, by sealing it up for some years, with phosphorus pentoxide in flasks made of resistance glass, its physical and chemical properties are found to be considerably

altered. The effect is most pronounced on the boiling points of liquids, which are increased in some cases by 60° C. The table below gives the variation in boiling point noted when substances have been intensively dried for a period of years :—

TABLE LVIII.—EFFECT OF INTENSIVE DRYING ON THE BOILING POINTS OF LIQUIDS

Liquid.	Period of drying (years).	Original b.p., °C.	New b.p., °C.	Rise in b.p., °C.
Mercury . . .	9	357	420	63
Ethyl alcohol . .	9	78·3	138	59·7
Bromine . . .	8	63	118	55
Methyl alcohol . .	9	65	120	55
Ether . . .	9	35	83	48
Propyl alcohol . .	9	97	134	37
Carbon tetrachloride .	9	78	112	34

When a solid is dried in a similar way, its melting point is increased, but the effect is not so marked.

TABLE LIX.—EFFECT OF INTENSIVE DRYING ON THE MELTING POINTS OF SOLIDS

Substance.	Normal m.p., °C.	New m.p., °C.	Rise in m.p., °C.
Sulphur trioxide (α).	50	61·5	11·5
Sulphur . .	112·5	117·5	5
Bromine . .	—7·3	—4·5	2·8
Iodine . . .	113	116	3

The explanation of this curious phenomenon is not easy to arrive at, as there are very conflicting statements in the scientific literature concerning it. The fact which does seem clear, however, is that when a liquid has been carefully dried it does not give a steady stream of vapour, unless it is heated to a temperature considerably above its boiling point, as usually determined. In these experiments, the bulb of the thermometer was placed in the liquid, and not in the vapour, as in the ordinary procedure. There are two possible explanations of this fact. (1) That some inner equilibrium is disturbed by the drying, thus giving rise to different properties.

(2) Something has happened to the surface of the liquid which prevents normal evaporation and encourages superheating.

A glance at the first explanation shows that it fits in very well with Smits' theory of allotropy. A liquid, like a solid, is supposed by Smits to consist of a complex mixture of various molecular types, all in equilibrium with each other. It is possible that drying alters this equilibrium, thus altering the general physical properties of the liquid. This would also explain the effect on the melting points of solids. This view is supported by the fact that during the drying the surface tension of the liquids rose continuously, reaching a value indicating an increased molecular weight according to the Ramsay and Young equation.

Further, Smits suggested that if a liquid which had been intensively dried were to be distilled it might be found that it could be fractionated into normal and associated liquids each having a different boiling point. It has been claimed that this has actually been demonstrated. Dried benzene when completely distilled gives a vapour coming over at different temperatures. If this is so, however, it is difficult to see why any ordinary liquid, like water, which is partially associated, does not show a similar fractionation, unless it be that the absence of water in the above cases not only alters the equilibrium, but prevents its re-establishment.

There are several facts which argue against Smits' theory. In the first place, it is hardly to be expected to be true on thermodynamic grounds, for it would mean that the addition of a very small amount of water to the intensively dried liquid produces an enormous effect, whereas further additions have not the slightest effect in the same direction. It is contrary to experience to find the addition of such a small quantity of water making such a profound change in the free energy of the system.

On kinetic grounds, too, it is highly improbable. The minute amount of water necessary to effect such a great change in properties throughout the whole liquid phase means that the water would have to exert some force far beyond the ordinary range of ordinary molecular forces. This could only happen by some transmitted effect for which there is no evidence.

Further, J. W. Smith has studied the rate of evaporation of ethyl bromide in a vacuum across a constant temperature gradient, and finds that it is retarded by intensive drying. The vapour pressure, however, remained unaltered, and there was no variation in the distillates. No fractionation had taken place as might have been expected if the inner equilibrium had been changed. Boiling occurred with considerably more difficulty in the intensively dried liquid. Observations of a similar kind have been made on the rate

of evaporation and condensation of ammonium chloride, with the same result. It seems extremely probable that the internal equilibrium in a liquid is not altered by intensive drying, but that the effects are due to some form of superheating, probably induced by the removal of nuclei, such as dust, or colloidal particles (it has been shown that the presence of colloidal particles hastens evaporation of a liquid) by the phosphorus pentoxide.

Within recent years much doubt has been cast on the validity of many of the earlier observations on intensive drying and some of them have actually been discredited. For examples, concerned with the properties of oxides of nitrogen when dried over phosphorus pentoxide, the student should consult the paper by Stoddart (J.C.S., 1945, 448).

145. Allotropes of Liquids.—It has been claimed that some liquids exist in allotropic forms, though these have never been isolated. From a study of curves illustrating the connection between temperature on the one hand, and various physical properties, such as dielectric constant, density, specific heat and viscosity, on the other, it has been argued that discontinuities which occur in the curves indicate the existence of distinct forms of these liquids. The liquids under consideration are nitrobenzene, carbon disulphide and ether, but further investigation has shown that the claims for nitrobenzene are not true. This may possibly be the case with the other liquids.

Recently it has been shown that liquid helium exists in two allotropic forms, with a transition point influenced by pressure.

If liquids do exist in allotropic forms, it would be necessary to assume that they possess a structure (§ 119).

It may be mentioned that liquid sulphur certainly exists in allotropes, though, from what has been said on p. 324, it will be realised that we are here dealing with a sol, *i.e.*, with two immiscible or partially miscible forms of the liquid.

146. Crystal Structure and Chemical Constitution.—Haüy, the founder of the science of crystallography, put forward the rule in 1784 that every definite chemical compound had its own crystalline form, but certain apparent exceptions to this statement were soon found. In the same year, it was noted that crystals of potash alum could contain a good deal of iron, and yet still retain their crystalline form. In 1816, Gay-Lussac grew a crystal of potash alum in a solution of ammonium alum, so that Haüy's Law did not appear to be correct. It seemed from this experiment that two substances had the same crystalline form, and this could not be so if Haüy's Law were true.

In 1819 Mitscherlich put forward his *law of isomorphism*, which

states that *substances possessing an equal number of atoms, united in a similar way, exhibit identity of crystalline form.*

This statement makes two provisions. There must be an equal number of atoms in the molecule, and these atoms must be united in a similar way. It is obviously conflicting with Haüy's Law, for according to him there is no such thing as identity of crystalline structure of two chemical compounds. Each compound has its own structure, irrespective of whether it is similar in composition to anything else or not, if Haüy's Law is correct.

Mitscherlich's Law of Isomorphism proved so useful in various ways in the development of chemistry (see p. 24) that its truth was not doubted, but more recently experiments have been carried out to see whether substances with similar chemical compositions actually do have identity of crystalline structure, and it has been found that the identity is not complete. There are minute differences in the crystal angles. No two substances have exactly the same crystalline structure. As an example, the two substances, ferrous sulphate, $FeSO_4.7H_2O$, and copper sulphate (Boothite), $CuSO_4.7H_2O$, may be quoted. These two compounds are definitely isomorphous. They satisfy all the criteria of isomorphism as laid down in the next section, but, as the table shows, there are slight differences in the dimensions of the unit cells and in the angle of the cell.

	a : b ·	
Copper sulphate, $CuSO_4.7H_2O$ . .	1·1622 : 1 : 1·5000	74° 24′
Ferrous sulphate, $FeSO_4.7H_2O$ . .	1·1828 : 1 : 1·5427	75° 44′

It is seen, then, that Haüy's Law is actually true, and that Mitscherlich's Law cannot be enforced too rigidly. There is another point, too, where Mitscherlich's Law has proved to be erroneous. It states that the substances showing isomorphism must contain equal numbers of atoms. Now, many substances are known which are isomorphous, and yet which have not the same number of atoms. An example that comes to mind at once is ammonium alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$, and potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$. The ammonium alum contains eight more atoms to the molecule than does potash alum, and yet the two are quite definitely isomorphous. There are many other cases of this.

Mitscherlich's Law, as it was first proposed, can hardly be called a law. It is therefore better to amend it, and merely say that substances which have similar chemical compositions frequently possess very similar crystalline forms.

147. Methods of Recognising Isomorphism.—Since complete identity of crystalline structure is not strictly a criterion of isomorphism, this method cannot be used to recognise it. There are some crystals which have crystalline constants quite similar to each other, yet they are not isomorphous. It is found, however, that if substances are isomorphous their crystal elements are closely similar, though the converse is not necessarily true.

The formation of *mixed crystals* is a good criterion of isomorphism. If two substances are isomorphous, it is possible to make crystals containing both of them in varying proportions. These crystals are called " mixed " crystals. As an example of their formation, copper sulphate and ferrous sulphate may be taken. If a solution containing these two substances is crystallised, it is always found that the copper sulphate crystals contain a certain amount of iron. Hence the difficulty of purifying copper sulphate by fractional crystallisation. The crystals always bring down with them some iron, and this can only be removed by treating the solution with strong nitric acid, which oxidises the ferrous sulphate to ferric sulphate, in which form it is no longer isomorphous with copper sulphate. It is then possible to crystallise the copper salt free from iron.

It is not all isomorphous crystals that are capable of forming mixed crystals. Two crystals may be isomorphous and yet be unable to do this. Thus, whilst the actual formation of mixed crystals is in general a good proof of isomorphism, the converse—that if substances are isomorphous they should form mixed crystals—is not true. The formation of mixed crystals appears to be governed by the molecular volumes of the substances. If these are close there is greater probability of the formation of mixed crystals.

Another method of deciding whether two substances are isomorphous is to see whether they will form isomorphous overgrowths with each other, *i.e.*, if one crystal will grow in a solution of another. Here, again, there are some exceptions. When two substances are chosen with almost the same molecular volumes, they may form overgrowths, and yet not be isomorphous.

It will be seen that none of these criteria, *viz.*, (1) similarity of crystalline form, (2) formation of mixed crystals, and (3) formation of isomorphous overgrowths, provides a perfectly complete test for isomorphism ; but if more than one of these is found to hold good for two solids, it may usually be taken that they are isomorphous.

148. Isopolymorphism.—Substances existing in more than one crystalline form may be isomorphous in each form with another compound also existing in more than one form. An example will make this clear. Arsenious oxide occurs in two forms, one octahedral and the other rhombic Antimonious oxide also exists in

two varieties, similar in crystalline form to the arsenious oxide crystals. The octahedral forms of the two oxides are isomorphous, as are also the rhombic forms. The oxides are said to be isodimorphous. There are several cases of isodimorphism known, and a few of isotrimorphism.

Another phenomenon sometimes referred to as isodimorphism is illustrated by the behaviour of the compound iodine bromide IBr, which is isomorphous on the one hand with iodine, and on the other with bromine.

149. Applications of the Phenomenon of Isomorphism.—Mitscherlich's Law of Isomorphism finds its greatest application in the determination of atomic weights, where it serves as an aid to the fixing of valency. Examples of its application to the determination of the atomic weights of vanadium, beryllium, zirconium, silver and selenium, have already been given in the section on atomic weights (§ 11).

150. Vapour Pressures of Crystals. — Every solid substance possesses a vapour pressure, though in the great majority of cases this is very minute. The fact that solids do possess this vapour pressure is evidenced by the fact that certain solids evaporate to quite a marked extent when left out in the open, whilst many solids possess a smell, which they would not have if no vapour were given off. Like the vapour pressures of liquids, that of a solid increases with temperature. It may reach atmospheric pressure before the solid melts, in which case sublimation occurs. In sublimation, the solid evaporates without melting, and is deposited on the cold sides of the vessel. It is clear that this is an analogue of distillation in the liquid state. The temperature at which the vapour pressure of a solid becomes equal to the external pressure is called the "sublimation point." Substances which sublime on heating cannot be melted unless an increased pressure is put upon them. If this is done, the vapour pressure has to reach a much higher value before the substance can "boil" away, and before this happens the melting point may be reached.

When a solid is sublimed, heat is absorbed analogous to latent heat of evaporation of a liquid. This is called the heat of volatilisation, and, at the sublimation point, it is equal to the sum of the latent heat of fusion and of evaporation.

SUMMARY

Solids are crystalline, *i.e.*, they are made up of an orderly assemblage of units. Their chief characteristics are rigidity and anisotropy. Some substances are known, however, which form "liquid crystals." These retain the anisotropic nature of ordinary crystals, but possess

little or no rigidity. The process of crystallisation depends on the formation and growth of crystal nuclei. These processes have been studied, and the effect of temperature upon them investigated. There is some doubt as to the existence of an amorphous state.

The structure of crystals has been investigated mainly by X-ray diffraction. The space lattice of the crystal acts as a three-dimensional diffraction grating towards X-rays, and, from the nature of the spectra obtained, the structure of the crystal can be elucidated. Laue used the crystal as a transmission grating; the Braggs used it as a reflection grating. Debye and Scherrer devised a powder method whereby it became unnecessary to use a large, single crystal of the substance. By these methods the distances between the planes in which the atoms lie can be found, and also the nature of the particles (where they are not atoms). Such X-ray analysis has revealed numerous facts about crystals, among which may be mentioned: (*a*) the difference between allotropic forms, *e.g.*, diamond and graphite, (*b*) the nature of threads, such as cellulose, (*c*) the fact that unstretched rubber is amorphous, whilst the stretched material is crystalline, (*d*) the nature of glass, and other vitreous substances, (*e*) confirmation of the tetrahedral carbon model, and the hexagonal benzene ring.

Electrons are also diffracted by crystals, and a beam of electrons may be used in a similar way to X-rays for determining crystal structure. This method has given valuable results in connection with the structure of films.

The atomic heats of solids do not all reach the value 6·4, as required by the law of Dulong and Petit, at ordinary temperatures. The law, however, is a limiting law. This is due to the fact that heat must be used up in breaking the crystal bonds. The law is true at low temperatures for soft substances, *e.g.*, lead, but not for hard ones, *e.g.*, diamond.

Many substances exist in a variety of crystalline forms. This phenomenon is known as polymorphism, in the case of compounds, and as allotropy, with elements. Polymorphs, and allotropes, differ in energy content. The metastable form contains the greater energy, and therefore has a higher vapour pressure and solubility. The temperature at which two forms of the same substance have equal stability is the transition point. There are three types of allotropy: (*a*) enantiotropy, or reversible allotropy, the allotropes being mutually interconvertible (*e.g.*, rhombic and monoclinic sulphur); (*b*) monotropy, or irreversible allotropy; one form may be converted into the other, but the reverse change is not brought about by a reversal of the conditions (*e.g.*, white and violet phosphorus); (*c*) dynamic allotropy; two forms exist in equilibrium (*e.g.*, the equilibria in liquid sulphur). There are several methods of determining transition points: (*a*) the thermometric method, making use of the heat evolved or absorbed on transition from one form to the other; (*b*) the dilatometric method, which makes use of the volume change at transition; (*c*) the vapour pressure method, which determines the temperature at which both forms have the same vapour pressure; (*d*) the solubility method; at the transition point both forms have the same solubility; (*e*) optical methods; (*f*) electrical methods.

When a substance is dried intensively, its physical and chemical properties are found to be altered. According to Smits' theory of allotropy, allotropy is due to an alteration in the internal equilibrium between various molecular aggregates in the solid. The effect of

intensive drying can be explained by supposing that the removal of water causes a shifting of this inner equilibrium.

Mitscherlich's Law of Isomorphism states that substances possessing an equal number of atoms, united in a similar way, exhibit identity of crystalline form. It is not perfectly true. The best criteria of isomorphism are, (*a*) similarity of crystalline form, (*b*) formation of mixed crystals, (*c*) formation of isomorphous overgrowths.

Crystals have definite vapour pressures, and when the vapour pressure reaches atmospheric pressure, at a temperature below the melting point of the substance, the crystal sublimes.

SUGGESTIONS FOR FURTHER READING

SMITS, A. "Theory of Allotropy." (*Longmans*, 1922.)

TUTTON, A. E. H. "Crystallography and Practical Crystal Measurement." (*Macmillan.*)

WYCKOFF, R. W. G. "The Structure of Crystals." (*Chemical Catalog Co.*, 1924.)

BRAGG, W. H., and BRAGG, W. L. "*X*-rays and Crystal Structure." (*Bell*, 1925.)

TUTTON, A. E. H. "Crystalline Form and Chemical Constitution." (*Macmillan*, 1926.)

FINDLAY, A. "The Phase Rule and its Applications." (*Longmans*, 1923.)

QUESTIONS

(1) How would you attempt to determine the molecular weight of a solid? How far can a solid be said to possess a molecular weight?

(2) How has the structure of crystals been investigated? Outline some of the important results that have arisen from this work.

(3) Define the term "allotropy." What classes of allotropy can be distinguished?

(4) Discuss the allotropy of nitrogen, sulphur, phosphorus, and hydrogen.

(5) In what ways does water influence the physical properties of liquids and solids, and how can this be accounted for?

(6) Discuss Smits' theory of allotropy.

(7) What energy considerations govern the existence of stable and metastable states, and how are these reflected in the physical properties of substances in the various states?

(8) What is meant by the term "isomorphism"? To what use can a study of this phenomenon be put?

CHAPTER VIII

CHEMICAL KINETICS AND EQUILIBRIUM

151. Velocity of Reaction.—Every chemical reaction under specified conditions of temperature, concentration, etc., proceeds at a definite speed. The majority of inorganic reactions, namely, those which take place between ions, proceed very rapidly, and would commonly be called instantaneous. Actually, however, they each have a definite speed. Most organic reactions, which take place between covalent compounds, proceed much more slowly.

The speed of a reaction may be defined as the weight of the reactants transformed, in gram-molecules, per second (see also § 162).

There are a number of factors which alter the speed of a reaction. They are temperature, concentration, and catalysis, although there may also be others, such as surface tension.

152. Reversible Reactions. The Nature of Equilibrium.—It has been known for some time that many chemical reactions do not go to completion as indicated by the equations representing them. Thus, when phosphorus pentachloride is heated in a closed vessel, the reaction

$$PCl_5 = PCl_3 + Cl_2$$

takes place; but the pentachloride is not entirely converted into trichloride and chlorine. At a certain stage in the process, the reaction stops and a mixture of pentachloride, trichloride, and chlorine is obtained. If some phosphorus trichloride, together with an equivalent quantity of chlorine, is heated in a closed vessel to the same temperature as the pentachloride in the first experiment, it will be found that some phosphorus pentachloride is formed, and, at the same temperature, the final composition of the mixtures in both experiments will be the same. It would therefore appear that the phosphorus trichloride is recombining with the chlorine as fast as the pentachloride is decomposing. When this occurs there is a state of equilibrium. Reactions which can proceed in both directions are called "reversible reactions."

Another common example of a reversible reaction is the action

of steam on red-hot iron. It is well known that hydrogen is prepared by this method, and that the residue is ferroso-ferric oxide, Fe_3O_4.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

If this reaction were to be carried out in a closed vessel, as it could, for example, if water were heated in an iron vessel which would withstand the pressure, it would be found that it does not proceed to completion, but that only a certain proportion of the water is converted into hydrogen. If the reverse reaction were carried out, at the same temperature as before, and under exactly the same conditions, it would be found that the composition of the equilibrium mixture would be the same. Hence, although the reaction comes to a standstill, this is only an apparent standstill. Actually the reactions are proceeding all the time, but the forward reaction is going on at exactly the same rate as the backward. There is thus no actual stoppage of the reaction. In the ordinary laboratory preparation of hydrogen by passing steam over red-hot iron, the back reaction is not permitted to occur, for the hydrogen is swept out of the apparatus by the oncoming steam, and prevented from reacting with the ferroso-ferric oxide formed. Similarly with many other reactions. It is necessary to take careful consideration of the conditions of a reaction before saying whether it will proceed in the forward direction, in the backward direction, or both simultaneously.

It has been said that all chemical reactions are reversible. This may be true if these reactions may be carried out under any chosen conditions, but the majority of chemical reactions, as they are performed in the laboratory, proceed in one direction only. The precipitation of barium sulphate by adding hydrogen sulphate to barium chloride, although it may appear to be irreversible, is certainly a reversible reaction, because if barium sulphate is treated with hydrogen chloride a small quantity of barium chloride and sulphuric acid may be produced. In carrying out reactions in the laboratory, one is careful to obtain the greatest yield of the substance required by so defining the conditions that the back action is minimised. Thus, in the preparation of an organic ester, it is well known that the action of an acid on an alcohol yields an ester and water, but that the ester may also be hydrolysed back to the acid and alcohol from which it was made by boiling with water. Here then we have a reversible reaction, but care is taken to get as great a yield of ester as possible in the reaction by removing the water from the ester as soon as it is formed. This is accomplished by adding to the reaction mixture some dehydrating agent, such as

zinc chloride, or concentrated sulphuric acid. In this way the back reaction is prevented.

Thus, whilst it is true that all chemical reactions may be made reversible by choosing the conditions correctly, so it is also true that a reaction may be made to proceed to completion, or very nearly so, by preventing the back reaction from taking place.

153. The Law of Mass Action.—The causes of chemical action attracted a number of the more thoughtful chemists in the late eighteenth century. The question of chemical affinity was beginning to be studied, in an empirical way, at this time, and in 1775, Bergmann published a "Table of Affinities." In this he showed that he realised that reactions could be reversible, and hence that affinities could actually be reversed. He published a list of "affinities of elements in fire," and "in water." In 1777, Wenzel suggested that the rate of a chemical reaction did not depend only on the affinities of the combining substances, but also on their quantity. This suggestion, which might have been very fruitful, was, however, ignored. In 1799, Berthollet explained the formation of sodium carbonate in certain Egyptian lakes by the interaction of calcium carbonate and sodium chloride. In the laboratory calcium chloride and sodium carbonate give a precipitate of calcium carbonate, and the solution contains sodium chloride. These two reactions are exactly the reverse of each other, but Berthollet maintained that the first could go on if the quantity of the sodium chloride, or of the calcium carbonate (in solution), were sufficiently large, and these conditions were found in these lakes. He stated that increase in mass could overcome weakness of affinity. He was, however, wrong in stating that the quantity of substance present could affect the ratio in which the substances combine. This was against the Law of Constant Proportions, which had just been propounded. Berthollet, however, did not believe in the truth of this law, as was mentioned in Chapter I. (p. 3).

Later, investigations were made of the rates of chemical reactions. Wilhelmy was the first to do this in 1850. In 1862, Berthelot and St. Gilles investigated the equilibrium between ethyl alcohol, acetic acid, ethyl acetate, and water, and arrived at conclusions which were embodied by Guldberg and Waage in their "Law of Mass Action," in 1864.

Guldberg and Waage stated that "*the rate at which a substance reacts is proportional to its active mass.*" The "*velocity of a chemical reaction is proportional to the products of the 'active masses' of the reactants.*"

What is meant by the "active mass" of the substance? The "active mass" was assumed by Guldberg and Waage to be pro-

portional to the molecular concentration in the case of gaseous and dissolved substances. The molecular concentration is the concentration expressed in gram-molecules per litre, and, since a gram-molecule of every substance contains the same number of molecules, concentrations expressed in this way indicate the number of molecules present.

Take the reaction,

$$A + B \rightleftharpoons C + D.$$

(The symbol $\rightleftharpoons$ indicates that the reaction is reversible.)
The velocity of the forward reaction is proportional to the molecular concentration of A and to that of B, and hence is proportional to their product. Molecular concentrations are represented by symbols in square brackets; thus [A] represents the molecular concentration of A. The velocity of the forward reaction is thus

$$V_f = k_1 [A] [B].$$

Similarly, the rate of the backward reaction is given by

$$V_b = k_2 [C] [D].$$

At equilibrium these two rates are the same, since as much of the products are formed as are decomposed in the same time; hence

$$V_b = V_f;$$

$$k_2 [C] [D] = k_1 [A] [B],$$

$$\frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]} = K.$$

K is called the *equilibrium constant* of the reaction, and k_1 and k_2 are called *velocity constants.*

154. Derivation of the Law of Mass Action on the Basis of the Kinetic Theory.—According to the kinetic theory, substances are made up of molecules in motion, and chemical combination does not occur unless two molecules collide. Combination does not take place at every collision. Many of them are quite ineffective. Not one collision in a million results in combination, in reactions which take place at a measurable speed. However, the number of effective collisions is a definite fraction of the total (p. 369).

It is clear that the number of collisions, and the number of effective collisions, will be increased, the greater the number of molecules present, *i.e.*, the greater the concentration. Thus, the rate of the reaction will be proportional to the molecular concentration of the reactant. Where reaction is taking place between two dissimilar molecular species, collision must occur between two molecules of the different types, and the probability of this will depend on the concentration of both. This probability will be given by the product of the two concentrations. Hence, the velocity of the reaction is

proportional to the product of the molecular concentrations of the two species, which is the Law of Mass Action.

The law may also be proved by thermodynamics.

155. Some Examples of the Application of the Law of Mass Action.—Consider first the rate of formation of ethyl acetate from ethyl alcohol and water. The equation is

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

Hence, the rate of formation of ethyl acetate and water is given by

$$V_f = k_1 [CH_3.COOH] [C_2H_5OH].$$

The reverse reaction will also go on, unless steps are taken to remove the water, or the ester, as it is formed. The rate of the reverse reaction is given by

$$V_b = k_2 [CH_3.COOC_2H_5] [H_2O].$$

At equilibrium the rates are equal; hence

$$V_b = V_f,$$

$$k_1 [CH_3.COOH] [C_2H_5OH] = k_2 [CH_3COOC_2H_5] [H_2O],$$

$$\therefore K = \frac{k_1}{k_2} = \frac{[CH_3COOC_2H_5] [H_2O]}{[CH_3.COOH] [C_2H_5OH]}.$$

The equilibrium constant is K.

It is usual to write in the numerator the active masses of the products, and in the denominator those of the reactants. The value of K for the above reaction is 4 at 25° C.

In all determinations of equilibrium constants care must be taken to see that the equilibrium does not alter during, or as a result of, the analysis of the equilibrium mixture. In many cases of reaction at fairly high temperatures the reactions will proceed very slowly at room temperature, so that sudden cooling of the reaction mixture will stop the reaction, and the proportions of the substances present will be those obtaining at the higher temperature. This is called "freezing the equilibrium." It may be mentioned in passing that this process is one of great importance. The only reason why endothermic substances like ozone are stable at room temperatures is because they are in such a state that the equilibrium has been frozen. Ozone is formed at very high temperatures. The passage of the silent discharge through oxygen is merely the addition of a large amount of energy to the oxygen, in another way than by direct heating. If oxygen, then, is heated to extremely high temperatures, some ozone will be formed. If the reaction mixture were to be cooled to room temperatures suddenly, the equilibrium would be frozen, and the amount of ozone present would be the same as if the gas were kept at the high temperature. Of course,

it is useless to bring about the cooling slowly, for this will allow time for the reactants to alter their equilibrium.

The combination of hydrogen and iodine to form hydrogen iodide has been studied by Bodenstein. All that is necessary is to heat the hydrogen and iodine together, in various proportions, in sealed tubes, to a temperature about 450° C. After a time, sufficiently long for equilibrium to be attained, the tubes are suddenly cooled, and the amount of hydrogen left determined by absorbing the iodine and hydrogen iodide in potassium hydroxide. The amount of hydrogen iodide and of iodine are determined in the liquid obtained by absorption by the usual methods of volumetric analysis.

In an actual experiment, it was found that when 20·55 gm.-mols. of hydrogen were heated to 445° C. with 31·89 gm.-mols. of iodine, the equilibrium mixture contained 2·06 gm.-mols. of hydrogen, and 13·40 gm.-mols. of iodine, and 36·98 gm.-mols. of hydrogen iodide. The reaction is

$$H_2 + I_2 \rightleftharpoons 2HI,$$

and the mass action equation is,

$$K = \frac{[HI]\,[HI]}{[H_2]\,[I_2]} = \frac{[HI]^2}{[H_2]\,[I_2]}.$$

Substituting the values

$$K = \frac{(36{\cdot}98)^2}{2{\cdot}06 \times 13{\cdot}40} = 49{\cdot}5.$$

Hence the equilibrium constant is 49·5.

Of course, if different initial concentrations are taken, different values for the quantities of substances formed will be obtained, but the equilibrium constant will still be the same at the same temperature. This can be tested by repeating the experiment with different quantities. The following are some of the results obtained.

TABLE LX.—THE HYDROGEN IODIDE EQUILIBRIUM (Bodenstein)

Initial Concentrations. gm.-mols.		Final Concentrations. gm.-mols.			K.
H_2	I_2	H_2	I_2	HI	
20·57	5·22	15·46	0·11	10·22	61·44
20·6	14·45	7·79	1·64	25·72	51·77
20·55	31·89	2·06	13·40	36·98	49·55
20·41	52·8	1·07	33·46	38·68	41·8
20·28	67·24	0·52	47·48	39·52	63·3

The values of K have been calculated from

$$K = \frac{[HI]^2}{[H_2][I_2]}.$$

Although K appears to vary considerably, the unavoidable experimental error is great. Any error in the concentration of hydrogen iodide is squared, so that the above figures indicate that the reaction follows the law.

If only the initial concentrations of hydrogen and iodine and the concentration of hydrogen iodide formed are known, the equilibrium constant can still be calculated. The procedure, which is quite general, is as follows. Consider the reaction

$$H_2 + I_2 \rightleftharpoons 2HI.$$

Let $2x$ gm.-mols. of hydrogen iodide be produced, and let a be the initial concentration of hydrogen in gm.-mols. per litre, and b the initial concentration of iodine in gm.-mols. per litre (at the temperature of the experiment the iodine will be in the vapour state). The volume of hydrogen iodide formed is not different from the total volume of the gases from which it was formed. Since $2x$ gm.-mols. of hydrogen iodide are produced for x gm.-mols. of hydrogen and x gm.-mols. of iodine used up, the final concentration of hydrogen will be $(a - x)$ and of iodine $(b - x)$ gm.-mols.

Substituting these values in the mass equation, we have

$$K = \frac{4x^2}{(a - x)(b - x)}.$$

If we know x, a and b, we can then calculate K. Thus taking as a numerical example the first set of data given in the table above :—

Initial concentration of hydrogen $= 20{\cdot}57 = a$.
Initial concentration of iodine $= 5{\cdot}22 = b$.
Concentration of hydrogen iodide at equilibrium $= 10{\cdot}22 = 2x$.

$$\therefore a - x = 20{\cdot}57 - 5{\cdot}11 = 15{\cdot}46$$
$$b - x = 5{\cdot}22 - 5{\cdot}11 = 0{\cdot}11$$
$$\therefore K = \frac{4x^2}{(a - x)(b - x)} = \frac{(10{\cdot}22)^2}{15{\cdot}46 \times 0{\cdot}11} = 61{\cdot}44$$

In examples involving gaseous equilibria, the concentrations of the reactants are frequently expressed as their partial pressures. It is clear that these are equivalent to the concentrations.

156. The Effect of Pressure on Chemical Equilibrium.—It is molecular concentration that enters into the mass equation. If pressure is applied to a system, the volume becomes smaller, and the molecular concentrations of the constituents are increased. If there is no volume change in the reaction, it is clear that the equili-

brium will not be altered in any way, for the concentrations of products and reactants will be affected in the same proportion; but, if there is a volume change in the course of the reaction, that reaction will be favoured which takes place with decrease in volume. This also follows from the principle of Le Chatelier, which states that if any constraint is applied to a system in equilibrium the equilibrium is shifted in such a way as to annul, or tend to annul, the constraint. In this case the constraint is the application of pressure. The reaction which results in decrease in volume will therefore take place, for by itself decreasing the volume the system tends to annul the effect of the pressure.

Consider the dissociation of phosphorus pentachloride. It takes place according to the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

Suppose there are initially a gram-molecules of phosphorus pentachloride in a volume V litres. The reaction is supposed to be carried out in closed vessels, so that V remains constant. If there are x gram-molecules of phosphorus trichloride formed, it follows from the equation that there will also be x gram-molecules of chlorine formed. The molecular concentration of the pentachloride at equilibrium will therefore be $(a - x)/V$, whilst that of the trichloride and of chlorine will be (x/V). Hence, applying the mass law,

$$K = \frac{\left(\frac{x}{V}\right)^2}{\frac{a-x}{V}} = \frac{x^2}{(a-x)\,V}.$$

It will be noticed that V occurs in the denominator. Hence the greater V is, the greater $\frac{x^2}{a-x}$ will be, for the constant K must be maintained. This means that the amount of dissociation, x, must be greater. Hence the diminution of pressure (*i.e.*, increase in volume, V, since it is only by increasing the volume that the pressure can be reduced without removing some of the reactants from the system) in this system results in an increase in the dissociation, and conversely.

Where V disappears in the mass equation, pressure, of course, has no effect on the equilibrium. Thus, in the dissociation of hydrogen iodide, there is no change in volume, and so V does not figure in the mass equation, and pressure alterations have no effect on the equilibrium.

This effect of pressure on the position of equilibrium is of great

importance in technical processes. In the Haber synthesis of ammonia, the reaction is,

$$N_2 + 3H_2 = 2NH_3.$$

Four volumes of the mixed nitrogen and hydrogen give only two volumes of ammonia. Hence the formation of ammonia will be favoured by the application of pressure, and in practice, in the Haber process, a pressure of 200 atmospheres is used, whilst in the Claude process a pressure of 1,000 atmospheres is employed.

In some cases it is found uneconomical to work at hign pressures, although better yields would result. Thus in the Contact process for the manufacture of sulphuric acid by making sulphur dioxide combine with oxygen, the reaction is

$$2SO_2 + O_2 = 2SO_3,$$

and involves a decrease in volume. Hence it would be favoured by the application of pressure. This is not done, however, in practice, owing to the difficulty of making acid-proof apparatus suitable for working at high pressures, and also because a sufficiently good yield may be obtained without recourse to the application of pressure.

A quantitative example of the effect of pressure on the equilibrium may be found in the Haber synthesis of ammonia. The effect of pressure on the yield of ammonia will be calculated. The reaction is

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

At a given temperature, let the partial pressures of nitrogen, hydrogen and ammonia in the equilibrium mixture be p_{N_2}, p_{H_2} and p_{NH_3}. Then, by the Law of Mass Action,

$$\frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} = K. \quad \therefore p^2_{NH_3} = K \cdot p_{N_2} \cdot p^3_{H_2} \quad . \quad . \quad . \quad . \quad (1)$$

Now double the pressure on the system. If it is assumed that the partial pressure of the ammonia is small compared with that of nitrogen and hydrogen and the small amount of extra ammonia formed does not affect the partial pressures of the other gases—a condition which always holds in technical practice—then the partial pressures of hydrogen and nitrogen will be doubled.

Let the new equilibrium pressures be p'_{N_2}, p'_{H_2} and p'_{NH_3}. Then

$$\frac{p'^2_{NH_3}}{p'_{N_2} p'^3_{H_2}} = K = \frac{p'^2_{NH_3}}{2p_{N_2} \cdot 8p^3_{H_2}}.$$

$$p'^2_{NH_3} = 16p_{N_2} \cdot p^3_{H_2} \cdot K = 16p^2_{NH_3}, \text{(see equation (1) above).}$$

$$\therefore p'_{NH_3} = 4p_{NH_3}.$$

Thus, the partial pressure of ammonia is four times what it was originally, although the pressure on the system has only been doubled. The amount of ammonia formed per unit volume of

nitrogen is $\frac{2p_{NH_3}}{p_{N_2}}$ in the first case, and in the second $\frac{2p'_{NH_3}}{p'_{N_2}}$. It will be seen that the yield is double, since $p'_{NH_3} = 4p_{NH_3}$ and $p'_{N_2} = 2p_{N_2}$.

157. Effect on the Equilibrium of Adding one of the Products of the Reaction.—To study this question, the dissociation of phosphorus pentachloride may again be considered. It is desired to find what effect there will be on the dissociation if chlorine is added from some outside source to the equilibrium mixture. Writing the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

suppose we have at equilibrium a gm.-mols. of the pentachloride in V litres, b gm.-mols. of trichloride, and b gm.-mols. of chlorine in V litres. It follows from the equation that the amounts of chlorine and of trichloride must be equal. The mass law gives

$$K = \frac{b^2}{aV}.$$

Suppose now that c gm.-mols. of chlorine are introduced into the system *without change of volume*. The concentration of chlorine is now $(b + c)$. Let b' and a' be the new concentrations of the trichloride, and pentachloride, respectively. Then,

$$K = \frac{b'(b + c)}{a'V}.$$

In order to maintain K constant, b must be decreased (to b'), and hence the dissociation will be retarded, some pentachloride being re-formed.

If, however, the chlorine is added with change of volume, it all depends on the volume change what the change in the system will be. If the volume after addition of chlorine is V', then the mass law states,

$$K = \frac{b'(b + c)}{a'V'},$$

where a' and b' are the new concentrations of pentachloride and of trichloride. It would be possible to work out the effect in any example in which the concentrations were given.

The effect of the addition of products of reaction on the position of equilibrium is well illustrated by the following experiment due to Gladstone. Consider the reaction

$$3KCNS + FeCl_3 \rightleftharpoons Fe(CNS)_3 + 3KCl.$$

The ferric thiocyanate is deeply coloured. Addition of potassium chloride in saturated solution (to avoid great changes in volume of the solution) makes the reaction mixture become appreciably paler.

This is due to the fact that the reverse reaction is favoured, since the value of $[Fe(CNS)_3]$ in the numerator of the mass action equation

$$K = \frac{[Fe(CNS)_3]\,[KCl]^3}{[FeCl_3]\,[KCNS]^3}$$

must become smaller to make K still constant. On the other hand, addition of ferric chloride causes a deepening of the colour, since the value of the denominator is increased, and consequently the value of the numerator must also be increased to maintain K constant. Similarly, addition of potassium thiocyanate also causes an increase in the depth of colour.

158. The Effect of Temperature on the Equilibrium.—According to Le Chatelier's principle (p. 346), in the case of a reversible reaction, increase in temperature will favour that reaction which takes place with absorption of heat. Decrease in temperature will favour the reaction which takes place with evolution of heat (see also p. 613).

It can be shown by thermodynamics (§ 321) that if K_1 and K_2 are the equilibrium constants of a reaction at absolute temperatures T_1 and T_2, and if Q_v is the heat of reaction expressed in gram-calories absorbed at constant volume,

$$\log_{10}K_2 - \log_{10}K_1 = -\frac{Q_v}{4{\cdot}576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

This equation may be made use of for determining the heat of reaction.

An example of the use of this equation is given on p. 351.

159. Some Numerical Examples.—In order that the reader may more fully comprehend the work that has just been described, he is recommended to try to work out the following numerical examples for himself. The solutions to the problems are also given below so that the work may be checked.

(1) The equilibrium constant in the reaction between ethyl alcohol and acetic acid to form ethyl acetate and water is 4 at 25° C. What weight of ethyl acetate will be obtained from 50 gms. of alcohol and 50 gms. of acetic acid, the reaction being carried out at 25° C. in a closed vessel ?

The equation is

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

According to the Law of Mass Action,

$$\frac{[CH_3COOC_2H_5]\,[H_2O]}{[C_2H_5OH]\,[CH_3COOH]} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the substances in square brackets stand for molecular concentrations.

It is supposed that the total volume of the system, V, does not

change during the reaction. Let x be the number of gram-molecules of ethyl acetate formed; then x will also be the number of gram-molecules of water formed.

The molecular weight of acetic acid is 60·05. Hence the molecular concentration of acetic acid was originally $\frac{50}{60{\cdot}05V}$. If x gram-molecules of products are formed, then x gram-molecules of reactants must have been used up, so the final molecular concentration of acetic acid was $\left(\frac{50}{60{\cdot}05} - x\right)/V$.

The molecular weight of ethyl alcohol is 46·047. Hence, final molecular concentration of alcohol is $\left(\frac{50}{46{\cdot}047} - x\right)/V$. Substituting these values in equation (1),

$$\frac{\left(\frac{x}{V}\right)^2}{\frac{\left(\frac{50}{46{\cdot}047} - x\right)\left(\frac{50}{60{\cdot}05} - x\right)}{V^2}} = K = 4.$$

$$\therefore \frac{x^2}{(1{\cdot}086 - x)(0{\cdot}8326 - x)} = 4,$$

$$\therefore x^2 = 4\,(0{\cdot}9038 - 1{\cdot}9186x + x^2),$$

or

$$3x^2 - 7{\cdot}6744x + 3{\cdot}6152 = 0.$$

The roots of this equation are

$$x = 1{\cdot}9747 \text{ or } 0{\cdot}5834.$$

The first of these is inadmissible, as the quantities of acetic acid and alcohol taken are insufficient to produce this amount of ethyl acetate, even if the reaction went to completion. Hence 0·5834 gm.-molecules of ethyl acetate will be produced, *i.e.*, 0·5834 × 88·0624 = 51·39 gms.

(2) Calculate the percentage dissociation of phosphorus pentachloride in an experiment in which 2·0 gms. of the substance were heated to 200° C. in a closed litre vessel, which contained only phosphorus pentachloride, and the products of the dissociation. The equilibrium constant for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

is 0·00793 at 200° C., and under the pressure developed in the experiment.

Suppose that initially the quantity of the pentachloride present was a gram-molecules. This dissociates, so that x gram-molecules

of both the trichloride and chlorine are formed, leaving $(a - x)$ gram-molecules of the pentachloride undissociated. As the reaction is carried out in a closed vessel, the volume, v, cannot change. By the Law of Mass Action,

$$\frac{x^2}{v(a - x)} = K.$$

Now, in the experiment, $a = \frac{2}{208 \cdot 255}$ gram-molecules per litre, $v = 1$, and $K = 0 \cdot 00793$.

$$\therefore \frac{x^2}{(0 \cdot 009603 - x)} = 0 \cdot 00793,$$

$$\therefore x^2 = 0 \cdot 00007615 - 0 \cdot 00793x,$$

or

$$x^2 + 0 \cdot 00793x - 0 \cdot 00007615 = 0.$$

The roots of this equation are $x = -0 \cdot 01305$ or $+0 \cdot 0056$.

The negative value is clearly inadmissible.

The percentage dissociation $= \frac{x}{a} \times 100 = \frac{0 \cdot 0056}{0 \cdot 009603} \times 100 =$ 58·32 per cent.

(3) The equilibrium constant of the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

at 528° C. is 980, and at 680° C. is 10·5. Find the heat of reaction.

The equation (§ 158) is

$$\log_{10} K_2 - \log_{10} K_1 = -\frac{Q_v}{4 \cdot 576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where K_2 and K_1 are the equilibrium constants at absolute temperatures T_2 and T_1, and Q_v is the heat of reaction at constant volume.

$$K_2 = 980\ ;\ K_1 = 10 \cdot 5\ ;\ T_2 = 801^\circ \text{ Abs.}\ ;\ T_1 = 953^\circ \text{ Abs.}$$

$$\log \frac{980}{10 \cdot 5} = \frac{-Q_v}{4 \cdot 576}\left(\frac{152}{801 \times 953}\right).$$

$$\therefore Q_v = \frac{953 \times 4 \cdot 576 \times 801 \times 1 \cdot 97}{152}$$

$$= 45{,}280 \text{ gm.-cals.}$$

The amount of heat *given out* is therefore 45,280 gm.-cals.

160. Application of the Law of Mass Action to Heterogeneous Systems.—Up to the present only those reactions which take place in one phase (*i.e.*, homogeneous reactions) have been considered. Many reactions, however, take place between reactants in different phases. These are called "heterogeneous reactions." Numerous reversible heterogeneous reactions are known. Indeed, one of

those quoted at the beginning of this chapter as an example of a reversible reaction, *viz.*, the action of steam on red-hot iron, is a heterogeneous reaction. The hydrogen and the steam are gases, whilst the other reactants are solids. Can the Law of Mass Action be applied to a reaction such as this ?

The easiest way to consider a reaction of this kind is to assume that it does go on in one phase only. Take the action of heat on calcium carbonate. This is a well-known reversible reaction. If calcium carbonate is heated in a closed vessel, a state of equilibrium is reached after a time, when no more calcium carbonate will decompose. This equilibrium is prevented in a lime-kiln, because it is open and the carbon dioxide can escape as it is formed.

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The reaction may be regarded as taking place between calcium carbonate and calcium oxide vapours, and carbon dioxide gas. The concentrations of the reacting substances will be expressed by their partial pressures. If these are p_{CaCO_3}, p_{CaO}, p_{CO_2}, the Law of Mass Action states

$$\frac{p_{CaO} \cdot p_{CO_2}}{p_{CaCO_3}} = K.$$

The partial pressure of calcium oxide is its vapour pressure. The vapour pressure of a solid is very small, but, at a given temperature, is constant so long as there is any solid present, so that both p_{CaO} and p_{CaCO_3} are constant, and the law gives us

$$p_{CO_2} = K'.$$

The system is therefore at equilibrium at a given temperature when a fixed pressure of carbon dioxide is present, a result which is also obtained from Phase Rule considerations (p. 391).

It may be taken as a general rule, when dealing with heterogeneous equilibria, that the active mass of a solid is constant.

The same considerations govern the dissociation of salt hydrates. Consider the reaction

$$CuSO_4 \ . \ 5H_2O \rightleftharpoons CuSO_4 \ . \ 3H_2O + 2H_2O.$$

If p_1, p_2, p_3, are the partial pressures of the pentahydrate, the trihydrate, and water vapour respectively in the system, then

$$\frac{p_2 \cdot p_3^2}{p_1} = K.$$

But the active masses of the solids are constant at a given temperature, so long as they both remain in the system.

Hence $$p_3^2 = k,$$
and $$p_3 = \sqrt{k} = k'.$$

This result has also been obtained from Phase Rule considerations (p. 394). As soon as one of the hydrates has disappeared, the conditions are altered, for a new equilibrium is set up, and then the partial pressure of the water vapour will be different from before, but will remain constant until the phases again change.

The dissociation of ammonium hydrosulphide, NH_4HS, is a slightly different case. This solid substance dissociates on heating into ammonia and hydrogen sulphide, two gases.

$$NH_4HS \rightleftharpoons NH_3 + H_2S.$$

If the partial pressures of the gases are p_{NH_3} and p_{H_2S} respectively, then the Law of Mass Action states

$$\frac{p_{NH_3} \cdot p_{H_2S}}{p_{NH_4HS}} = K.$$

But p_{NH_4HS} is the vapour pressure of the solid, and is constant as long as any solid is present. Hence

$$p_{NH_3} \cdot p_{H_2S} = k'.$$

This equation can be tested by adding one or other of the gases to the system and noting the effect on the equilibrium pressures. The following table gives results of such an experiment :—

TABLE LXI

p_{NH_3}	p_{H_2S}	$p_{NH_3} \times p_{H_2S}$
mm. 250·5	mm. 250·5	mm.[2] 62,750
208·0	294·0	61,150
453·0	143·0	64,780

The volume was kept constant. The product is reasonably constant.

161. Theory of Activities.—In the Law of Mass Action the quantities used are the active masses, which have been stated to be proportional to the molecular concentrations of the reactants. Owing to inter-molecular influences, the freedom of the molecules is always somewhat restricted in actual systems, and the active masses are not proportional to the molecular concentrations. It has therefore been proposed to substitute for the molecular concentration the "activity" of the substance. The activity is a thermodynamic function introduced by G. N. Lewis, and was at first purely formal.

As a result of work on electrolytes (§ 274) it is, however, now assuming more precise significance.

The activity coefficient f is defined as the factor by which the molecular concentration must be multiplied in order that the Law of Mass Action may be obeyed. The activity coefficient is always less than unity. There are several methods of determining activities, but further discussion of the question is beyond the scope of this book. The concept has found its greatest application in connection with ionic equilibria (§ 274).

162. The Order of a Reaction.—The next few sections will be concerned mainly with reaction velocity, and not with reversible reactions. The velocity of reaction is defined as *the rate of change of concentration of the reactants.* The order of a reaction is defined as *the minimum number of molecules necessary for the reaction to take place.* Thus in the reaction

$$lA + mB + nC \rightarrow aX + bY + cZ,$$

the velocity is given by

$$v = [A]^l [B]^m [C]^n,$$

and the order is the sum of the indices, $l + m + n$. The order of a reaction only has significance when it is applied to a reaction proceeding in one direction. It is quite possible for a reversible reaction to have two orders, one for the forward, the other for the backward reaction.

163. Unimolecular Reactions.—Unimolecular reactions are those in which the reaction velocity is proportional to the first power of the concentration of the reacting substance. They are not so common as they were at first thought to be. Many so-called "unimolecular" reactions were found not to be homogeneous reactions at all, but to take place at the walls of the vessel, or at the surface of some catalyst (see p. 357).

A unimolecular reaction may be represented by the equation

$$A \rightarrow B + C + \ldots$$

If there are present originally a gram-molecules per litre of A, and, after a time t, x gram-molecules are transformed, then the concentration after time t is $(a - x)$. Hence, by the Law of Mass Action.

$$v = \frac{dx}{dt} = k(a - x),$$

or

$$\frac{dx}{a - x} = kdt,$$

which on integration gives,

$$-\log_e (a - x) = kt + C,$$

where C is a constant.

To determine C, it is noted that when $t = 0$, $x = 0$. Substituting these values in the equation, we have

$$-\log_e a = C,$$

$$\therefore k = \frac{1}{t}\log_e \frac{a}{a - x}.$$

k is, of course, the *velocity constant.*

This equation governs all unimolecular reactions. It will be seen that the time taken to complete any definite fraction of the reaction is independent of the concentration. Thus, the time taken for the reaction to reach the half-way stage is found by putting $x = 0{\cdot}5a$. When this is done,

$$k = \frac{1}{t}.\log_e 2,$$

which does not involve the concentration.

The number of unimolecular gaseous reactions is very small, and at one time the view was put forward that they did not exist at all. However, a few have now been discovered. They are nearly all confined to molecules of rather complex structure. Until 1925 the only unimolecular reaction known was the thermal decomposition of nitrogen pentoxide. This decomposition is usually expressed in inorganic text-books by the equation

$$2N_2O_5 = 2N_2O_4 + O_2,$$

but, if it is unimolecular, this cannot be the primary change, since this equation involves the participation of two molecules of the substance. The mechanism of the reaction must therefore be somewhat as follows :—

$$N_2O_5 = N_2O_3 + O_2.$$

The nitrogen trioxide then decomposes immediately into nitric oxide and nitrogen dioxide :—

$$N_2O_3 = NO + NO_2.$$

The nitric oxide now immediately reacts with the pentoxide :—

$$NO + N_2O_5 = 3NO_2.$$

The above explanation is that suggested by Hinshelwood. There seems to be no reason, however, why the reaction should not take place as follows :—

$$N_2O_5 = N_2O_4 + O,$$
$$O + O = O_2.$$

The first of these reactions would be comparatively slow, and the second very rapid. It is the slow reaction that decides the speed of the complete change.

This reaction was first studied from the kinetic point of view by

Daniels and Johnston, by measuring the pressure after various time intervals. In order to be certain that the reaction was not catalysed by the walls of the vessel (in which case it would be heterogeneous), glass wool was introduced into the reaction vessel, but no variation in the velocity constant was found. Such a variation would obviously be expected if catalysis occurred. Reactions catalysed by the walls of the vessel are frequently called "wall-reactions."

The thermal decomposition of phosphine, PH_3, was considered for some time to be a homogeneous unimolecular reaction, but was shown by Hinshelwood and Topley to be a wall-reaction. By varying the amount of surface, the reaction was shown to be heterogeneous up to a temperature of 1,044° Abs. at least.

The thermolysis (thermal decomposition) of certain organic molecules seems to provide a number of unimolecular reactions. Thus the thermal decomposition of acetone at about 500° has been investigated by Hinshelwood and Hutchison (1926), who found it to be a homogeneous unimolecular reaction. The acetone breaks down primarily into carbon monoxide and two methyl groups, which then interact to give various hydrocarbons. The time of half-change was found to be independent of pressure over a wide pressure range. The reaction was investigated manometrically.

The thermal decomposition of propionaldehyde provides a similar unimolecular reaction. It gives carbon monoxide and a mixture of hydrocarbons consisting mainly of ethane and methane. At higher pressures, the time required for the completion of any definite fraction of the reaction is independent of the initial pressure, *i.e.*, of initial concentration. At lower pressures the velocity constant falls (see p. 373).

The thermal decomposition of dimethyl ether takes place according to the equation

$$CH_3 . O . CH_3 = [CH_4 + HCHO] = CH_4 + CO + H_2.$$

Here there is intermediate formation of formaldehyde, but this can be allowed for in the manometric determination of the rate of reaction. The reaction is unimolecular. A similar reaction is the action of heat on diethyl ether :—

$$C_2H_5 . O . C_2H_5 = CO + 2CH_4 + 0{\cdot}5\, C_2H_4,$$

which has also been shown to be unimolecular. Here, again, the constant falls at low pressures.

The racemisation of pinene in the gaseous state is a reaction which has been studied polarimetrically by Smith, and is found to obey the unimolecular law. The breakdown of azomethane, according to the equation

$$CH_3 . N : N . CH_3 = C_2H_6 + N_2,$$

has also been studied, and found to be homogeneous and unimolecular. A similar unimolecular change is found in the decomposition of azoisopropane, which takes place as follows :—

$$C_3H_7 . N:N . C_3H_7 = N_2 + C_6H_{14}.$$

The reaction

$$C_3H_7 . N:N . C_3H_7 = N_2 + C_3H_6 + C_3H_8$$

also takes place to a small extent.

An inorganic reaction which has been studied in this connection is the decomposition of sulphuryl chloride

$$SO_2Cl_2 = SO_2 + Cl_2.$$

This reaction is peculiar in being homogeneous in vessels made of Pyrex glass, yet heterogeneous in vessels of ordinary soda-glass. There seem to be two simultaneous reactions, one homogeneous and the other heterogeneous, going on under these conditions.

164. Pseudo-unimolecular Reactions.—All the unimolecular reactions already referred to take place in the gaseous phase, and it has been pointed out how comparatively rare a truly homogeneous reaction of this kind is. A few examples of homogeneous unimolecular reactions taking place in the liquid phase are known, but here again, they are uncommon.

Many reactions *appear* to give a unimolecular constant, *i.e.*, they obey the equation derived above for this type of reaction, yet they are not truly unimolecular. Consider what happens in a reaction such as the hydrolysis of ethyl acetate

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH.$$

If a large excess of water is used in this reaction, the amount of it used up in the hydrolysis is small compared with its total mass, and consequently its active mass does not suffer greatly by the change, and can be regarded as constant. Applying the mass law,

$$v = k[CH_3 . COOC_2H_5] [H_2O].$$

If $[H_2O]$ is constant,

$$v = k'[CH_3 . COOC_2H_5].$$

Thus, the equation is of the form of that for a unimolecular reaction, the only difference being in the value of the velocity constant k.

This is a general rule, and must be carefully borne in mind. Many reactions of the second order may be made to appear unimolecular by taking one of the reactants in great excess.

Another example of a reaction of this kind is the rate of inversion of cane-sugar. This is brought about by dilute solutions of acids (or alkalis), and also by enzymes, but takes place according to the equation,

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}.$$

It is clear that this change should be bimolecular, and not unimolecular, but in dilute solution the active mass of the water does not alter appreciably, and so the unimolecular law is obeyed. This reaction is a particularly suitable one to study, because it can be followed so easily. The reason why the reaction is called "inversion" is because the cane-sugar itself is optically active (p. 260), rotating the plane of polarisation of light to the right (dextrorotatory), whilst the resulting mixture of glucose and fructose is lævo-rotatory. The reaction can therefore be followed by means of the polarimeter, an instrument for measuring the amount of rotation of the plane of polarisation of light (p. 262). The rotation is measured at various intervals. The experimental details for carrying out this experiment are given at the end of the chapter. If the initial rotation is r_a, and the rotation after a long while, r_∞, and r_x the rotation after time t, then the amount of sugar remaining unchanged at time t is proportional to $r_x - r_\infty$.

Hence $$k = \frac{1}{t}\log_e\frac{r_a - r_\infty}{r_x - r_\infty} = \frac{2\cdot303}{t}\log_{10}\frac{r_a - r_\infty}{r_x - r_\infty}.$$

This reaction has been tested by various investigators, and the figures obtained by Lewis are given below :—

TABLE LXII.—INVERSION OF CANE-SUGAR IN 0·9 N-HCl at 25° C.

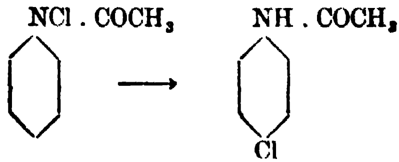
Time, mins.	Rotation, r_x.	Change of Rotation, $r_x - r_\infty$.	Velocity Coefficient, k.
0·0	+ 24·09° (r_a)	+ 34·83°	—
7·18	21·405	32·145	0·01118
18·00	17·735	28·475	0·01117
27·05	15·00	25·74	0·01118
36·80	12·40	23·14	0·01123
46·00	10·02	20·76	0·01125
56·07	7·80	18·54	0·01125
68·02	5·455	16·155	0·01129
101·70	0·30	11·04	0·01129
∞	− 10·74	—	—

It is seen that the velocity constant calculated on the basis of the above formula is reasonably constant, and so it is inferred that the reaction obeys the unimolecular law.

A reaction of the same type as the above is the mutarotation of glucose. When a solution of glucose is freshly prepared it is found to have a specific rotation of about 105° for the sodium D line. After standing, however, the rotation falls to about half this value, *viz.*, 52·5°. It is quite by chance that it happens to be about one-

half for glucose, other sugars giving quite a different ratio. This phenomenon is called mutarotation, and is due to a reversible isomeric change of α- into β-glucose. This proceeds as a unimolecular reaction. It is included as a pseudo-unimolecular reaction, as it appears to be catalysed by hydrogen and hydroxyl ions (p. 596), which may take some part in the reaction.

Another reaction which gives a first order constant, and is easily studied, is the isomeric change of N-chloroacetanilide into *p*-chloroacetanilide.



This change takes place in the presence of hydrochloric acid which acts as a catalyst. Actually the hydrochloric acid undergoes change during the reaction and is re-formed, as the following equations show.

$$C_6H_5.NCl.COCH_3 + HCl \rightleftharpoons C_6H_5.NH.COCH_3 + Cl_2;$$
$$C_6H_5.NH.COCH_3 + Cl_2 \rightleftharpoons ClC_6H_4.NH.COCH_3 + HCl.$$

Thus, the change will correspond with the unimolecular formula. The reaction is very easily followed, since the N-chloroacetanilide will liberate iodine from potassium iodide. Thus, by determining the amount of standard thiosulphate required by the solution, after adding excess of potassium iodide, the amount of unchanged substance can be determined. This is done at various intervals of time. Full details for carrying out this experiment are given at the end of the chapter. Below are given some results which show that the unimolecular law is obeyed by this reaction.

TABLE LXIII.—RATE OF TRANSFORMATION OF N-CHLOROACETANILIDE (BLANKSMA)

Time, mins.	Titration, $a - x$.	$k = \frac{1}{t} \log_e \frac{a}{a - x}$.
0	49·3	—
60	35·6	0·00543
120	25·75	0·00542
180	18·5	0·00545
240	13·8	0·00531
360	7·3	0·00531
480	4·8	0·00542

The catalytic decomposition of hydrogen peroxide is a reaction of the first order as regards results, though not so in theory. The catalyst may be platinum black, or hæmase. This reaction is very easily studied. The volume of oxygen evolved at different times after the reaction has started may be determined by carrying out the reaction in a flask attached to a gas-burette. Another method is to withdraw samples of the liquid from time to time and determine the amount of hydrogen peroxide left by titration with permanganate. This experiment is described on p. 377.

Why do we make a distinction between homogeneous unimolecular reactions and those which give the unimolecular constant but take place at the surface of a catalyst? Such a reaction is, for example, the decomposition of nitrous oxide at the surface of gold, or platinum. This gives the unimolecular constant. Hinshelwood and Green found that the decomposition of nitric oxide at the surface of a hot platinum wire was also unimolecular. The reason for putting these reactions in a different class is because they are just as much pseudo-unimolecular reactions as those already studied (p. 357). The active mass of the reacting substance is that in the layer adsorbed on the catalyst (p. 703), and not that in the gaseous phase. The concentration in the gaseous phase is not always proportional to the concentration in the adsorbed layer. Consider the thermal decomposition of nitrous oxide, which is, under certain conditions, a wall-reaction, *i.e.*, takes place on the walls of the containing vessel, and is due to adsorption of the gas on the walls. If the adsorption is small, all the adsorbing places on the glass surface will not be covered, and the adsorption will be proportional to the pressure, and so also will the reaction. In this instance the order of the reaction measured is its true order. But suppose that the pressure is greater, and the adsorption is therefore greater, and all the adsorbing places are full. Then further increase of pressure does not bring any more gas in contact with the catalyst, and the rate of the reaction ceases to be proportional to the pressure, and although the heterogeneous reaction is in reality a unimolecular reaction, it does not obey the unimolecular law. Similar considerations govern reactions of other orders.

165. Bimolecular Reactions.—In these reactions the concentrations of two molecular species may vary, or two molecules of the same species may disappear as a result of the reaction. The reaction may be written, in the general case, as

$$A + B \rightarrow C + D + E + \ldots.$$

Assume first that the initial molecular concentrations of A and B are the same, and call them a. After a time t, suppose that x gram-

molecules of both A and B have been transformed into C and D Then, according to the Law of Mass Action,

$$v = k(a - x)^2,$$

or,

$$\frac{dx}{dt} = k(a - x)^2.$$

Integrating this equation,

$$k = \frac{1}{at} \cdot \frac{x}{a - x} \quad \ldots\ldots\ldots \quad (1)$$

Consider the more general case, where the initial concentrations of A and B are not the same, but different, and equal to a and b respectively. Let x gram-molecules be converted after time t. Applying the Law of Mass Action,

$$\frac{dx}{dt} = k(a - x)(b - x).$$

Integrating,

$$k = \frac{1}{t(a - b)} \log_e \frac{b(a - x)}{a(b - x)}.$$

It will be noticed that as the concentrations appear in the denominator as a product, and in the numerator only as a single term, the value of the constant obtained will depend upon the units in which the concentrations are expressed. This was not so in the case of unimolecular reactions.

The time for half-change is calculated in a way similar to that used for unimolecular reactions. In equation (1), put $x = \frac{1}{2}a$.

$$k = \frac{1}{t} \cdot \frac{\frac{a}{2}}{a \cdot \frac{a}{2}} = \frac{1}{at}.$$

$$\therefore t = \frac{k'}{a}.$$

It is seen that for bimolecular reactions the time for half change is not independent of the initial concentration.

Bimolecular reactions are the most common, but the number which are known to proceed in a straightforward manner is still small. A few examples of them, with their methods of investigation, may be given.

The hydrolysis of ethyl acetate is a bimolecular reaction. It has already been pointed out that this reaction may become apparently unimolecular when the quantity of the hydrolysing agent is very great. If, however, ethyl acetate is hydrolysed by means of caustic soda, and the latter is not taken in such great excess that its activ-

mass may be assumed to be constant, it will be found that the bimolecular equation is satisfied. The reaction is

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH,$$

and it is obvious that as the reaction proceeds the caustic soda is progressively used up, and, by determining the amount of it left at any given stage, the rate of the reaction may be obtained. A dilute solution of ethyl acetate is therefore mixed with an equivalent quantity of sodium hydroxide solution (in order to make use of equation (1) (p. 361), and thus simplify the calculation), and measured volumes of the liquid are withdrawn at definite intervals, immediately passed into excess of standard acid to prevent any further reaction, and the excess of acid is determined by standard alkali. The concentration of sodium hydroxide found is also a measure of the amount of ethyl acetate used up. For full experimental details see p. 377. In all experiments on reaction velocity, it is necessary to maintain the reaction mixture at a definite temperature throughout, since the value of k is greatly altered by change in temperature. This is done by keeping the reacting mixture in a thermostat regulated for a suitable temperature. In this case a temperature of 25° C. is convenient.

A table of results is given below. It shows how the bimolecular constant is obtained, and that the results fail to agree with the unimolecular formula.

TABLE LXIV.—HYDROLYSIS OF ETHYL ACETATE

$a = 16{\cdot}00$

mins.	x.	Unimolecular, $k = \frac{1}{t}\log_e \frac{a}{a-x}$.	Bimolecular, $k = \frac{1}{at}\cdot\frac{x}{a-x}$
5	5·76	0·0893	0·0070
15	9·87	0·0640	0·0067
25	11·68	0·0524	0·0069
35	12·59	0·0442	0·0066
55	13·69	0·0352	0·0067

The reaction between hydrogen and iodine to form hydrogen iodide, and the reverse reaction, are both straightforward bimolecular reactions and have been exhaustively studied by Bodenstein. In the decomposition of hydrogen iodide, the gas was sealed in glass bulbs at 0° and at 760 mm. pressure, and these were then heated

for a known time in a thermostat arranged for high temperatures, usually a vapour bath.

Here the calculation is somewhat more complicated, because the reaction is reversible. The two reactions, the forward and back reactions, must be considered, and if x is the fraction of the hydrogen iodide decomposed in time t, then

$$\frac{dx}{dt} = k(1-x)^2 - k'\left(\frac{x}{2}\right)^2,$$

where k is the velocity constant of the forward reaction, and k' that of the back reaction.

Let y be the fraction decomposed at equilibrium ; then

$$k(1-y)^2 = k'\left(\frac{y}{2}\right)^2,$$

$$\therefore\ k' = \frac{k \cdot 4(1-y)^2}{y^2},$$

$$\therefore \frac{dx}{dt} = k(1-x)^2 - k \cdot \frac{4(1-y)^2}{y^2} \cdot \frac{x^2}{4},$$

$$\therefore kt = \frac{y}{2(1-y)} \log_e \frac{x(1-2y)+y}{y-x}.$$

Thus, k can be calculated from a knowledge of the amount decomposed at time t, and the amount decomposed at equilibrium. A similar method can be used for the reverse reaction.

Another bimolecular reaction is the decomposition of ozone,

$$2O_3 = 3O_2,$$

although the evidence in this case is rather conflicting. Hinshelwood states, however, that there seems to be no doubt that this reaction is a truly homogeneous bimolecular reaction.

The thermal decomposition of nitrous oxide $2N_2O = 2N_2 + O_2$ is bimolecular in the homogeneous state, and unimolecular in the heterogeneous state. It has been investigated by Hinshelwood and Burk. They measured the rate of the reaction by observing the increase of pressure during the change. Silica vessels were employed, and the reaction was proved to be homogeneous by showing that addition of silica powder made no difference to the rate.

166. Termolecular Reactions and Reactions of a Higher Order.— In this case the concentrations of three molecular species vary during the change, or three molecules of the same species enter into reaction. Termolecular reactions are rather rare. This is easily understood when the reaction mechanism is considered in terms of the kinetic theory. According to this theory, collision is necessary for reaction to take place. For a bimolecular reaction, two molecules

have to collide, and this is quite a likely thing; hence the greater number of bimolecular reactions. In a termolecular reaction, however, three different molecules have to come together at one and the same time, and the chance of their doing this is rather small. It must depend upon the length of time two of the molecules will remain in contact. It is obvious that very few reactions of a higher order still can be expected, though a few are known.

In deriving the expression for the velocity constant of a termolecular reaction, suppose that the three reactants have the same initial concentration a, and that after time t an amount x of them has been transformed. Then by the Law of Mass Action

$$\frac{dx}{dt} = k(a - x)^3,$$

$$\therefore \frac{dx}{(a - x)^3} = kdt,$$

$$\therefore k = \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}.$$

The time for half change is given by putting $x = \frac{a}{2}$.

$$k = \frac{1}{t} \cdot \frac{1}{2} \left(\frac{1}{\left(\frac{a}{2}\right)^2} - \frac{1}{a^2} \right)$$

$$= \frac{1}{2t} \frac{3}{a^2} = \frac{3}{2} \cdot \frac{1}{a^2t}.$$

$$\therefore t = \frac{3k'}{2a^2}.$$

When the initial concentrations are different the calculation is rather more complicated, and will not be given here.

The reduction of ferric chloride by stannous chloride is stated by Noyes to be a termolecular reaction. It can be written

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The reaction was followed by mixing equivalent solutions of stannous chloride and ferric chloride in a flask kept in a thermostat, and withdrawing quantities from time to time, the time being noted. These were run into mercuric chloride to destroy excess of stannous chloride, and then the ferrous iron was determined with dichromate. Secondary reactions take place easily, and the constancy of the velocity constant is not very satisfactory, as the following table of results shows.

TABLE LXV.—REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE (NOYES)

t mins.	x.	$k = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\}$.
1	0·01434	87
3	0·02664	87
7	0·03612	84
11	0·04102	87
40	0·05058	85

$a = 0·0625.$

Another termolecular reaction investigated by Noyes and Cottle was the action of sodium formate on silver acetate,

$$2AgOOC.CH_3 + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa.$$

167. Summary of Equations for Reactions of Various Orders.—(1) *Unimolecular.*

$$k = \frac{1}{t}\log_e\frac{a}{a-x}.$$

Time for half change,

$$t = \frac{\log_e 2}{k}.$$

(2) *Bimolecular.*—(*a*) Initial concentrations of all reactants the same,

$$k = \frac{1}{at}\cdot\frac{x}{a-x}.$$

Time for half change,

$$t = \frac{k'}{a}.$$

(*b*) Initial concentrations of reactants different,

$$k = \frac{1}{t(a-b)}\log_e\frac{b(a-x)}{a(b-x)}.$$

(3) *Termolecular.*—Initial concentrations of reactants the same,

$$k = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\}.$$

Time for half change,

$$t = \frac{3k'}{2a^2}.$$

168. Complications occurring in the Determination of Orders of Reactions.—The number of reactions which proceed strictly accord-

ing to the equations derived is very small, when the enormous number of chemical reactions that can take place is considered. The disturbing factors are chiefly: (1) the occurrence of the back reaction, (2) the occurrence of consecutive reactions, and (3) side reactions. *The effect of the back reaction* has already been considered in the thermal decomposition of hydrogen iodide, and will not again be discussed (p. 363).

Consecutive Reactions.—In some cases one reaction follows another. The equation then does not give much help in deciding the order of the reaction. The speed of such a reaction, which is made up of two or more parts, is that of the slowest reaction. Where a reaction is made up of two reactions, one of which is fast and the other slow, the kinetic treatment may not indicate the fast reaction at all. These consecutive reactions usually occur in solution, and there is often a great deal of uncertainty as to the mechanism of them.

As an example of a series of consecutive reactions, Lapworth's investigation of the bromination of acetone in the presence of hydrogen ions may be quoted. The chemical equation representing the complete change is

$$CH_3COCH_3 + H^+ + Br_2 \rightleftharpoons CH_3COCH_2Br + 2H^+ + Br^-.$$

The velocity of this reaction is proportional to the concentration of acetone and of hydrogen ions, but is unaffected by the concentration of bromine. This can be explained as follows: The acetone, in the presence of hydrogen ions, is transformed into an enol form :—

$$CH_3CO.CH_3[+ H^+] \rightleftharpoons CH_3.C(OH) : CH_2 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

This is a slow reaction.

The enol form rapidly adds on bromine,

$$CH_3.C(OH) : CH_2 + Br_2 = CH_2Br.C(OH)Br.CH_3 \quad . \; . \quad (2)$$

and the compound produced immediately loses hydrobromic acid,

$$CH_2Br.C(OH).Br.CH_3 = CH_3COCH_2Br + HBr \quad . \; . \; . \quad (3)$$

Reactions (2) and (3) are instantaneous, whereas reaction (1) is slow. The speed of the total change will be dependent largely upon the speed of the slowest link in the chain. Hence reaction (1) is the change, the speed of which governs that of the complete reaction. This explains why the concentration of the bromine does not affect the rate of the reaction.

Another example, studied by Noyes and Scott (1896), is the reaction between hydrogen peroxide and hydriodic acid. Iodine is liberated according to the equation

$$H_2O_2 + 2HI = I_2 + 2H_2O.$$

This reaction proved to be bimolecular, although the equation indicated that it should be termolecular. This was explained by supposing that the mechanism was

$$H_2O_2 + I^- = H_2O + IO^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$IO^- + I^- + 2H^+ = H_2O + I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The first reaction proceeds with measurable slowness, but the second is instantaneous. The first equation, therefore, decides the kinetics of the reaction. It may be mentioned that, as the second reaction is one of the fourth order, it, too, probably consists of a series of consecutive reactions.

Side Reactions.—When substances react, a number of independent reactions may take place, giving rise to different end products. Usually one of these reactions predominates, and is called the "main reaction," the others being called the "side reactions." It is usually possible by altering the conditions of experiment to make one or other of the side reactions assume the *rôle* of main reaction. In applying the Mass Law to examples of this kind, it is necessary to take each reaction separately, as if it occurred separately from the others, and connect the set up at the end, though this is, of necessity, a somewhat complicated process.

169. Methods of determining the Order of a Reaction.—The first method is to carry out the reaction and analyse the products from time to time, and then substitute the values in the various order equations (p. 365), and see which one fits the experimental data the best. This is the method most frequently used.

The second method is to determine the time required for a given fraction of the reaction to be completed, say, one-half of it. It will be seen from the equations given on p. 365 that the time for half change for reactions of different orders is inversely proportional to the concentration raised to the power of the order minus one. Thus, the time for half change is independent of concentration for a unimolecular reaction, whilst it is inversely proportional to the concentration for a bimolecular reaction, and inversely proportional to the square of the concentration for a termolecular reaction. Thus, if the times at which the reaction is half completed, t_1 and t_2, are determined for respective initial concentrations of c_1 and c_2, the equation connecting these times is

$$\frac{t_2}{t_1} = \left(\frac{c_1}{c_2}\right)^n,$$

where n is the order.

As an example of this, the figures for the thermal decomposition of phosphine are given below (Hinshelwood)

TABLE LXVI.—THERMAL DECOMPOSITION OF PHOSPHINE

Initial pressure, mm.	Half-life, secs.
707	84
79	84
37·5	83

Since the times are constant for various initial pressures, the reaction must be unimolecular. It is actually a heterogeneous reaction.

The third method is known as Ostwald's Isolation Method. In this, each reactant is taken in large concentration in turn, and the order of the reaction determined by the first method. The active mass of the substance taken in great excess may be taken as constant. The sum of the orders, when each reactant is separately taken in excess, is the order of the reaction. The method may be illustrated by the reaction between sodium formate and silver acetate, to which reference has already been made (p. 365).

$$2CH_3COOAg + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa$$

When the silver acetate is taken in large excess, its active mass remains constant, and the reaction is found to be unimolecular with respect to the sodium formate. When the latter is taken in excess it is found to be bimolecular with respect to the silver acetate. Hence the reaction is termolecular.

170. The Temperature Coefficients of Chemical Reactions.—The velocity of most chemical reactions varies greatly with temperature. The ratio of the velocity constants at two temperatures separated by 10° C., usually 25° C. and 35° C., is called the "temperature coefficient" of the reaction. It is, as a rule, numerically between two and three. The value of the temperature coefficient is of great importance in deciding the mechanism of chemical reactions (p. 369).

171. The Mechanism of Chemical Change.—Reactions take place between molecules, and, in order that there may be interaction between one molecule and another, there must be collision between them. It is highly unlikely that action could take place at a distance.

What happens when this collision takes place? Consider the two types of molecules—those in which there is an electrovalent linkage, and those in which there is a covalent linkage. It has been pointed out, in the chapter on valency (p. 168), that the bond between sodium and chlorine in sodium chloride is weak, because it

is an electrovalent linkage. As soon as common salt is dissolved in water it ionises, and the bond is broken. It is otherwise with covalent molecules (p. 168). These retain their individuality in solution. When silver nitrate and sodium chloride are brought together, silver chloride is precipitated according to the equation

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

The reactions $NaCl = Na^+ + Cl^-$, and $AgNO_3 = Ag^+ + NO_3^-$ have occurred before the solutions are mixed, and the reaction is $Ag^+ + Cl^- = AgCl$. The rate of this change is therefore determined by the rate at which the chlorine and silver ions can reach, and attach themselves to, the silver chloride lattice. Consequently, the reaction is almost instantaneous. The bond between the atoms is so weak that it can hardly be regarded as a bond at all, and so the ions have to overcome only a small force when they move to the silver chloride lattice.

The covalent linkage is stronger, and the breaking away of parts of such a molecule involves the performance of work against the linkage, and so reactions between covalent compounds are usually much slower than those between electrovalent compounds.

The simplest theory of the mechanism of chemical reactions would be that when molecules collide combination occurs, and that every collision is effective in producing combination. That this is not true is readily shown by considering the data obtained experimentally for a bimolecular reaction, such as the hydrogen iodide decomposition (p. 344). It is thus found that the number of molecules colliding is many millions of times the number which actually combine. Another reason for believing that all collisions are not effective is that, if they were, calculations based on the kinetic theory would indicate that the temperature coefficients of all reactions should be 1·04, whereas, as a general rule, they are considerably higher than this.

It is clear, then, that molecules which do react when they collide must be in some special state which favours combination. For this, the molecules might have to be orientated in some suitable way, or they might have to wait their turn to come into contact with a catalyst, or perhaps they might have to be activated by the acquisition of a certain amount of energy. It is this last assumption that has proved most fruitful in elucidating the nature of chemical change.

If E is the amount of energy that has to be present in a molecule for combination to take place with another molecule on colliding, it can be shown from the kinetic theory that

$$\frac{\text{number of effective collisions}}{\text{total number of collisions}} = e^{-E/RT},$$

where e is the base of natural logarithms, R is the gas constant, and T the absolute temperature.

Now, consider a reversible reaction, the velocity of the forward reaction being k, and that of the reverse reaction k'. Let the equilibrium constant be K. This is equal to k/k'. The effect of temperature on the equilibrium constant K is given by the expression

$$\frac{d \log_e K}{dT} = \frac{Q_v}{RT^2},$$

where Q_v is the heat of reaction (see p. 640).

Since
$$\log_e K = \log_e k - \log_e k',$$
$$\frac{d \log_e k}{dT} - \frac{d \log_e k'}{dT} = \frac{Q_v}{RT^2},$$
$$\therefore \quad \frac{d \log_e k}{dT} = \frac{A_1}{RT^2} + B,$$
$$\frac{d \log_e k'}{dT} = \frac{A_2}{RT^2} + B,$$
where
$$A_1 - A_2 = Q_v,$$
and A_1 and A_2 are energies.

The quantity B may or may not be independent of temperature, but Arrhenius showed empirically that the variation of the velocity constant k with temperature is given by the equation

$$\frac{d \log_e k}{dT} = \frac{A}{RT^2}.$$

A has the dimensions of energy.

The total number of collisions between molecules can be shown to be

$$Z = \sqrt{2}\pi\sigma^2 u n^2,$$

where σ = molecular diameter,
u = root-mean-square velocity of molecules,
and n = number of molecules per c.c.

The velocity constant of a reaction is proportional to the number of effective collisions, *i.e.*, proportional to the total number of collisions multiplied by $e^{-E/RT}$, *i.e.*, $\sqrt{2}\pi\sigma^2 u n^2 e^{-E/RT}$ . . . . . (1).

Now the value of $\sqrt{2}\pi\sigma^2 u n^2$ does not vary greatly with temperature. At least, its variation is negligible compared with that of $e^{-E/RT}$, and so $\sqrt{2}\pi\sigma^2 u n^2$ may be regarded as constant for different temperatures. Hence,

$$k = Ce^{-E/RT}.$$

On taking logarithms and differentiating, we have

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2},$$

which is of the same form as the Arrhenius equation mentioned above, and shows that the minimum energy required for effective collisions, which may be called the "*energy of activation,*" is identical with the A of the Arrhenius equation, and can therefore be calculated directly from the temperature coefficient of the reaction.

Thus, in Hinshelwood and Burk's experiments on the thermal decomposition of nitrous oxide, it was found that at a temperature of 1,125° Abs., $\log_{10} (k \times 10^3)$, where k is the velocity constant, was 4·064, and at 1,085° Abs., the value was 3·575. The Arrhenius equation states

$$\frac{d \log_e k}{dT} = \frac{A}{RT^2}$$

or

$$\log_{10} k_1 - \log_{10} k_2 = -\frac{A}{R \times 2{\cdot}303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= -\frac{A}{4{\cdot}576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Substituting the data above,

$$4{\cdot}064 - 3{\cdot}575 = -\frac{A}{4{\cdot}576}\left(\frac{1}{1{,}125} - \frac{1}{1{,}085}\right)$$

$$0{\cdot}489 = +\frac{A}{4{\cdot}576}\left(\frac{40}{1{,}125 \times 1{,}085}\right)$$

$$\therefore \quad A = +\frac{4{\cdot}576 \times 1{,}125 \times 1{,}085 \times 0{\cdot}489}{40}$$

$$= +\ 68{,}260 \text{ gm.-cals.}$$

Hence the energy of activation is 68,260 gm.-cals.

The meaning of the positive sign is that this is the amount of energy which the molecules must have *in excess of* the ordinary amount.

The applications of these principles are well shown by a calculation due to Lewis and quoted by Hinshelwood. It concerns the thermal decomposition of hydrogen iodide, and the object is to calculate the energy of activation from the Arrhenius equation, and then use this in the equation (1) above. In this way, the absolute velocity of the reaction can be calculated. If it agrees fairly well with experimental data it may be taken that the method is correct.

The temperature coefficient of the reaction gives a value for A, and therefore of E, of 44,000 calories.

It is now required to find the total number of effective collisions from the equation

$$Z = \sqrt{2}\pi\sigma^2 u n^2 e^{-E/RT}.$$

The molecular diameter of hydrogen iodide may be taken as $3{\cdot}5 \times 10^{-8}$ cm. Suppose the concentration of hydrogen iodide is one gram-

molecule per litre, then the number of molecules per c.c. will be $6{\cdot}1 \times 10^{20}$, since Avogadro's number is $6{\cdot}1 \times 10^{23}$. At 556° Abs., the root mean square velocity is $3{\cdot}3 \times 10^4$ cm. per sec. The value of $\sqrt{2}\pi\sigma^2 un^2 e^{-E/RT}$ is therefore

$$\sqrt{2}\,.\,\pi\,.\,(3{\cdot}5 \times 10^{-8})^2\,.\,(6{\cdot}1 \times 10^{20})^2 e^{-\frac{44{,}000}{1{,}112}}\,.\,3{\cdot}3 \times 10^4$$
$$= 3{\cdot}25 \times 10^{14} \text{ per c.c.}$$

This is the number of collisions between activated molecules per second in 1 c.c. of gas. The number of molecules which should react per litre is therefore $3{\cdot}25 \times 10^{17}$. To express this as a fraction of a gram-molecule we divide by Avogadro's number, as follows,

$$\frac{3{\cdot}25 \times 10^{17}}{6{\cdot}1 \times 10^{23}} = 5{\cdot}3 \times 10^{-7}.$$

This is the fraction of a gram-molecule reacting in one second, when the concentration of gas is one gram-molecule per litre, and so it is the velocity constant k, in gram-molecules per litre per second. The experimental value at 556° Abs. is $3{\cdot}5 \times 10^{-7}$, which is in quite satisfactory agreement, considering our uncertainty as to molecular diameters.

This indicates that the theory of energy of activation is essentially correct.

Difficulties are, however, experienced when unimolecular reactions are considered. In the case of these reactions, the decomposition cannot be due to collision followed by immediate breakdown, otherwise the reaction would be bimolecular. However, collisions previously received may have put the molecule into an unstable state, and cause it to undergo transformation later.

Some amount of activation must be supposed to take place in such systems, since the temperature coefficient is always so much greater than it should be according to the kinetic theory.

The theory of unimolecular reactions was investigated by Perrin in 1919. He stated that, since the rate of a unimolecular reaction is independent of the pressure, it ought to be possible to expand a gas to infinity and still have the same rate of reaction. The molecules, being at an infinite distance apart, will never collide with each other, and consequently cannot receive energy to activate them. Perrin therefore suggested that the molecules were activated by the absorption of radiation from some external source.

This theory seemed to offer a very neat explanation of the cause of chemical action, and was further developed by W. C. McC. Lewis, but is not now generally held. There is nothing illogical in the theory, for photochemical reactions are brought about by the absorption of radiation, and the Einstein Law of the Photochemical

Equivalent gives a satisfactory explanation in many cases (see p. 721). It has been found possible, however, to explain unimolecular reactions on the theory of activation by collision, as will be shown below, and so there is no further need for the radiation hypothesis. Also, the calculated frequency of radiation necessary to accelerate a reaction is found by experiment to be quite inactive as a general rule. Numerous other objections have also been raised. Many attempts have been made to modify the original radiation theory to make it satisfy the experimental data, and a theory combining both activation by collision and by radiation has been proposed; but, although there is nothing inherently impossible in the theory, it seems better to use the collision theory alone.

Lindemann was the first to show that it really was possible for the molecules taking part in a unimolecular reaction to receive their energy of activation by collision, if it could be assumed that reaction did not take place at once when the molecule had been activated, but that a certain period of time elapsed. Activated molecules can give up their additional energy to molecules poor in energy on colliding with them. It is assumed that in their motion molecules pass through periods of maximum and minimum stability, and Lindemann supposes that the molecule is activated by collision, but does not undergo transformation until it passes through its next minimum of stability. If the time that elapses between reception of energy and transformation is large compared with the time between two impacts, most of the activated molecules will lose their energy again by another collision before they have time to break down. Hence, the rate of activation and the rate of transformation are quite different.

The number of activated molecules will be proportional to $e^{-E/RT}$ (p. 369), but only a small number of these decompose; most of them are deprived of their energy by other collisions. Hence, the chemical reaction does not disturb the number of active molecules very much. The factor $e^{-E/RT}$ is independent of pressure, and the number of reacting molecules is a definite small fraction of this, so this too will be independent of pressure. Hence, the conditions required for a unimolecular reaction are satisfied.

Let us now consider what will happen, on this theory, at low pressures. It is clear that this theory does not get over Perrin's objection as to non-activation at infinite dilution. But, consider what will happen at moderately low pressures. Here the time between the collisions will be much greater; sufficient, in fact, to allow many more of the activated molecules to go through their positions of minimum stability and break down before they collide with other molecules. Hence, as the pressure is reduced, there

must be a point when the unimolecular constant begins to alter. Nearly all unimolecular reactions studied (§ 163) show this.

Another method of explaining unimolecular reactions, involving activation by collision, is that of Christiansen and Kramers. They state that the products of the reaction, which possess both the chemical heat of reaction and the heat of activation originally associated with the molecule before decomposition, immediately activate fresh undecomposed molecules by collision. Thus, every activated molecule which is decomposed passes on energy and ensures the production of new activated molecules. Hence, Lindemann's conclusion is reached, that the number of activated molecules is not reduced by the occurrence of the reaction, though the Christiansen-Kramers explanation appears the more satisfactory.

When the products of reaction begin to accumulate in the system, however, there will be more inert molecules with which the activated products can collide, which will merely mean a loss of activating energy. Active molecules will thus be deactivated if they collide with inactive molecules of product, or with some added molecules with which reaction does not take place, *e.g.*, some foreign gas, like hydrogen, helium or nitrogen. The theory could be tested by adding some foreign gas to the reaction mixture and seeing if the velocity of the reaction decreased. This has been done for nearly all the unimolecular reactions studied, with no effect. This favours Lindemann's theory as opposed to Christiansen-Kramers'.

To overcome this difficulty, the latter made the assumption that the active products could only activate molecules of the reactant, and not of any inert gas, or the inactive products. Theoretically this is not such an unreasonable assumption as it appears. Nevertheless, most of the evidence is in favour of the Lindemann theory.

The ways in which energy is taken up by molecules in activation has not been dealt with, but it may be stated that this process must always be governed by the quantum theory. Most available evidence shows that the vibrational motion of the molecule is of the most importance in chemical action. The quantum theory of chemical reaction regards the energy of activation as an energy "hump" which must be exceeded by the reacting molecules. The theory has been used to predict successfully the absolute value of the velocity of chemical changes in simple cases, and gives a more accurate picture than the classical theories.

SUMMARY

The speed of a reaction is the amount of the reactants transformed, in gram-molecules, per second. According to the Law of Mass Action, the rate of a reaction is proportional to the product of the active masses (or of the molecular concentrations) of the reactants. Chemical

reactions usually occur in both directions, unless the conditions are so arranged that the back reaction cannot take place. When equilibrium is attained, the rate of the forward reaction is equal to that of the back reaction. In the reaction

$$mA + nB + \ldots \rightleftharpoons xP + yQ + \ldots,$$

the speed for the forward reaction is

$$v_1 = k_1[A]^m [B]^n \ldots,$$

and that of the back reaction is

$$v_2 = k_2 [P]^x [Q]^y \ldots,$$

where the symbols in square brackets represent molecular concentrations. At equilibrium, $v_1 = v_2$, and, therefore,

$$k_1 [A]^m [B]^n \ldots = k_2 [P]^x [Q]^y \ldots,$$

and $$K = \frac{k_1}{k_2} = \frac{[P]^x [Q]^y}{[A]^m[B]^n} \ldots .$$

k_1 and k_2 are called "velocity constants," and K the "equilibrium constant."

The effect of pressure, and of addition of one of the products of the reaction to the system at constant volume, may be predicted from the above equation. In some instances, the "active-mass" of a substance is not proportional to its molecular concentration. It is then necessary to use "activities" instead of molecular concentrations. These are defined to be proportional to the active mass.

The order of a reaction is the least number of molecules necessary for the reaction to take place. The order of the reaction whose mechanism is represented by

$$lA + mB + nC = aX + bY + cZ + \ldots .$$

is $l + m + n$. The equations governing the reactions of various orders are given on p. 365. Unimolecular reactions are rare. The majority are thermal decompositions of organic molecules. They are usually investigated manometrically. There are a number of reactions which obey the unimolecular law, and yet are not true unimolecular reactions, as some second substance, of which the active mass does not alter appreciably, enters into the reaction. This second substance is frequently a catalyst. The order of a reaction may be determined by the following methods: (*a*) by seeing whether the experimental data agree with one or other of the formulæ; (*b*) by finding how the time required to complete a given fraction of the reaction depends upon the concentration of the reactants; (*c*) by taking the reactants separately in excess, and finding the order according to (*a*). The sum of the orders thus found is the order of the reaction. Side reactions and consecutive reactions often complicate the work.

Chemical change depends upon the collision of molecules. Only those possessing a certain amount of energy, called "energy of activation," will decompose. The number of effective collisions, which is only a minute fraction of the total number of collisions, can be calculated, and hence the absolute velocity of the reaction can be obtained. This agrees well with that observed experimentally. The energy of

activation, E, is connected with the velocity constant k, and the temperature T, by the expression

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2}.$$

Unimolecular reactions also proceed owing to activation by collision, but, according to Lindemann's theory, decomposition does not take place immediately after collision. The molecules have positions of maximum and minimum stability, and only decompose in the latter condition. Hence, before attaining this, they may be deactivated by another collision.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 15.—To study the equilibrium between ethyl alcohol, acetic acid, ethyl acetate and water.

Set up a thermostat for 60° C. Draw off three test-tubes, and place in them (1) about 3 gms. of absolute alcohol, and 1 gm. of glacial acetic acid; (2) 2 gms. of glacial acetic acid, and 2 gms. of absolute alcohol; (3) 3 gms. glacial acetic acid, and 1 gm. of absolute alcohol. Seal off the tubes and place them in the thermostat for a day. Remove them from the thermostat and break them open under water. Titrate each solution with normal caustic soda. Also titrate a known weight of glacial acetic acid with the same solution. Calculate the concentrations of acid, alcohol, ester and water at equilibrium, and see if they obey the Mass Law. (Theory, p. 361.)

Experiment 16.—To study the rate of transformation of N-chloroacetanilide into *p*-chloroacetanilide.

First prepare some N-chloroacetanilide by the following method. Suspend a weighed quantity of acetanilide in excess of a solution of potassium bicarbonate and add the calculated quantity of bleaching-powder solution which has been standardised against thiosulphate. Extract the product with chloroform, and recrystallise from a mixture of chloroform and petroleum ether; m.p. 91° C. Set a thermostat for 25° C. Dissolve 16–20 gms. of the N-chloroacetanilide in 100 c.c. of 20 per cent. acetic acid in a small flask, which is then corked and placed in the thermostat. One hundred c.c. of a normal solution of hydrochloric acid in a similar flask are also placed in the thermostat. When the two flasks have attained the temperature of the thermostat (an interval of half an hour should be allowed), the two solutions are mixed and the time taken. Immediately withdraw 5 c.c. of the solution and run it into an excess of acidified potassium iodide, and titrate the liberated iodine with standard thiosulphate. Further portions of 5 c.c. are withdrawn at intervals of 10, 20, 30, 45, 60, 90 and 120 minutes, and the above procedure repeated. Calculate the amount of substance left after each time. This will be $(a - x)$. Calculate the amount at time 0, this will be a. Actually, there is no need to calculate the absolute concentrations, since the titrations are proportional to these. See whether the results best fit the bimolecular, or the unimolecular, equation. (Theory, p. 359.)

Experiment 17.—To study the rate of inversion of cane-sugar.

Dissolve 20 gms. of cane-sugar in water, and make up to 100 c.c. Prepare also a normal solution of hydrochloric acid. Put two flasks,

containing 50 c.c. of each solution respectively, in a thermostat set for 25° C., and when they have attained this temperature, mix the solutions and pour into a polarimeter tube, which can be surrounded by a water jacket, through which flows water at 25° C. Take the rotation as soon as possible, and then at intervals of five minutes for half an hour, then at intervals of fifteen minutes. Take a final reading after the tube has been allowed to stand for two or three days. This gives r_∞. Calculate the values of $r_x - r_\infty$, and work out the constant from the equation

$$k = \frac{1}{t}\log_e\frac{r_a - r_\infty}{r_x - r_\infty} = \frac{2{\cdot}303}{t}\log_{10}\frac{r_a - r_\infty}{r_x - r_\infty}.$$

(Theory, p. 358.) Pure sugar should be employed.

Experiment 18.—Investigate the rate of decomposition of hydrogen peroxide.

Hydrogen peroxide does not decompose at an appreciable rate at ordinary temperatures without the addition of a catalyst. A suitable catalyst is colloidal platinum, which is easily prepared by sparking between two platinum wires under water (or see p. 667).

Take about 50 c.c. of " 20 volume " hydrogen peroxide and make up to 1 litre. Take 100 c.c. of this in a conical flask and place in the thermostat at 25° C. Add 2 c.c. of colloidal platinum, and withdraw 5 c.c., mix it with excess of dilute sulphuric acid and titrate with N/20 permanganate. Note the time at which the withdrawal was made, and take further quantities of 5 c.c. at intervals of five minutes, or at increasing intervals. Calculate the amount of hydrogen peroxide left at each time, and see whether the data obtained fit the unimolecular equation. Instead of calculating the concentration the actual titre may be used. To obtain the initial concentration, titrate some of the original solution with the permanganate before adding the catalyst.

The effect of temperature on this decomposition may also be studied by repeating the experiments with a further quantity of hydrogen peroxide placed in a thermostat regulated for a different temperature. If the temperature is now made 35° C., the temperature coefficient may be obtained. (Theory, p. 360.)

Experiment 19.—To study the rate of hydrolysis of ethyl acetate by an alkali.

Prepare some N/2 sodium hydroxide solution free from carbonate. The solution must be kept free from air, and may be used in an automatic burette (see A. J. Mee, *School Science Review*, December, 1933). After standardising this, measure out enough to prepare 250 c.c. of N/10 sodium hydroxide in a measuring flask, and make up to the mark. Dissolve 4·4 gms. of freshly distilled ethyl acetate in 500 c.c. boiled distilled water. This will make an N/10 solution. Put 200 c.c. of each solution in separate conical flasks capable of holding 500 c.c., and put both in the thermostat at 25° C. Whilst these are attaining the temperature of the bath, measure out 25 c.c. of N/10 hydrochloric acid into five small conical flasks. Now mix the ethyl acetate and the sodium hydroxide thoroughly, take the time, withdraw 25 c.c. and run it into the acid in one of the small flasks. This immediately stops the reaction. The time should be taken when the pipette is half empty. Now titrate the excess of acid by means of N/10 sodium hydroxide free from carbonate. Take out other portions at intervals of a quarter of an hour.

Calculate the velocity constant from the bimolecular equation. (Theory, p. 361.)

Experiment 20.—Examine the reaction between sodium formate and silver acetate.

Prepare N/10 solutions of sodium formate and of silver acetate, and standardise them by the usual methods. Set a thermostat for 80° C. Take 100 c.c. of each solution in separate conical flasks, and allow them to attain the temperature of the thermostat. The flasks should be securely corked. Mix, and note the time. Withdraw 10 c.c., run it into cold potassium thiocyanate (50 c.c. of N/10), and note the time when the pipette is half empty. Titrate the excess thiocyanate with standard silver nitrate. Calculate the concentrations of formate and acetate left, and see if the reaction follows the termolecular equation,

$$k = \frac{1}{2t} \cdot \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}.$$

(Theory, p. 365.)

Experiment 21.—Determine the order of the reaction $6HI + HBrO_3 = HBr + 3H_2O + 3I_2$.

This is done by determining the time taken to complete a given fraction of the reaction. Prepare N/10 solutions of potassium iodide, potassium bromate, and hydrochloric acid, and an N/100 solution of thiosulphate.

In a 350-c.c. conical flask place 25 c.c. of the iodide solution and 100 c.c. of acid, and add 100 c.c. of water. In another similar flask place 25 c.c. of bromate solution, and put both flasks in the thermostat at 25° C. When both have attained the temperature of the bath, mix, and note the time of mixing. At intervals of two, and later five, minutes, take out 25 c.c. of the mixture, run it into 50 c.c. of ice-cold water to stop the reaction. Determine the amount of iodine by titration with thiosulphate.

Now prepare another solution with only half the concentration of bromate, *i.e.*, 50 c.c. iodide, 200 c.c. of hydrochloric acid, and 225 c.c. of water and 25 c.c. bromate. Repeat the observations with this mixture.

From the results of the titrations, calculate the number of gram equivalents of hydrogen iodide used up. Plot these against the time in minutes, and find the time taken for, say, one-third of the hydrogen iodide to be oxidised in both cases.

The product of the concentration of the reactants in the first case is twice that in the second, and so, if the reaction is bimolecular, the time required for any definite fraction of the reaction to be completed should be twice as great in the second case as in the first. See whether this is the case. (Theory, p. 361.)

SUGGESTIONS FOR FURTHER PRACTICAL WORK

Investigate the following :—

(*a*) The reduction of ferric chloride by stannous chloride.

(*b*) The order of the reaction in the case of hydrolysis of methyl acetate by means of an acid catalyst.

(*c*) The temperature coefficient of the hydrolysis of ethyl acetate by sodium hydroxide.

(*d*) The mutarotation of glucose

(e) The catalytic decomposition of hydrogen peroxide using the gas burette to determine the volume of oxygen evolved in a given time.

(f) The order of the reaction given under (a) by taking excess of the reagents in turn.

SUGGESTIONS FOR FURTHER READING

HINSHELWOOD, C. N. "Kinetics of Chemical Change in Gaseous Systems." (*Oxford University Press*, 1941.)

Consult the original papers mentioned in this book. They will give a valuable insight into the difficulties of this work, which cannot be gone into here. For a discussion of the Radiation Theory, see the Faraday Society discussion on "Radiation and Chemistry," *Trans. Faraday Soc.*, 1922, 546. Papers by the chief exponents of this theory—Perrin and McC. Lewis—were given. See also the Chemical Society Discussion on "The Critical Increment of Homogeneous Reactions" held on December 17th, 1931.

QUESTIONS

(1) What do you understand by a reversible reaction? Give examples of such reactions.

(2) What contributions were made to chemistry by Berthollet, Berthelot, and Guldberg and Waage? State the Law of Mass Action, and show how it may be derived qualitatively from the kinetic theory.

(3) What are the factors which influence chemical equilibrium? Illustrate your answer by examples.

(4) The ammonia in equilibrium with a 1 : 3 nitrogen-hydrogen mixture at 50 atmospheres and 400° C. is 25 per cent. by weight. Calculate the equilibrium constant.

(5) In the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$, the equilibrium constant is 198 at 430° C. Calculate the percentage conversion of a gas containing 50 per cent. sulphur dioxide, 40 per cent. oxygen, and 10 per cent. nitrogen at this temperature.

(6) The equilibrium constant in the reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ at various temperatures is given in the table below.

T° Abs.:	1811	1877	2033	2580	2675
K:	0·0092	0·0105	0·0161	0·0539	0·0590

Calculate the heat of the reaction and the percentage yield of NO in the process if conducted at 2,000° C.

(7) Illustrate the importance of the Law of Mass Action in technical processes.

(8) What do you understand by the order of a reaction? Show how you would determine the order of the reaction between methyl alcohol and acetic acid.

(9) What is a unimolecular reaction? Give examples of this type of reaction. What explanation of them has been given?

(10) Give an account of the radiation theory of chemical reaction, and explain its defects.

(11) What is meant by heat of activation? How can it be determined?

(12) What is the importance of a knowledge of the temperature coefficient of a chemical reaction?

(13) The following data have been obtained for the thermal decomposition of malonic acid, which takes place according to the equation

$$CH_2(COOH)_2 \longrightarrow CH_3COOH + CO_2.$$

t, min. . .	10	20	35	56	∞
Pressure, mm. .	37·0	67·0	108·0	155·0	302·0

Find the order of the reaction. All the reactants are in the vapour phase. (The data are due to Hinshelwood.)

(14) The following data have been obtained for the reaction between acetic anhydride and water. (Sidgwick and Rivett.)

$a = 0{\cdot}1160$

$t = 0$ . .	87	417	544	852 secs.
$x =$	0·02378	0·07748	0·08848	0·10360

a is the quantity of acetic anhydride present initially, and x that used up at time t after the commencement of the reaction, both quantities in gram-molecules. Find the order of the reaction, and whether it agrees with the chemical equation. If not, attempt an explanation.

(15) How would you attempt to find the order of the reaction between chloroform and alcoholic potash? What result would you expect to find, and why?

(16) The following results for the velocity constant of the reaction

$$2N_2O_5 = 2N_2O_4 + O_2,$$

were found by Daniels and Johnston.

Temp. ° C.	65°	45°	25°	0°
k	0·292	0·0299	0·00203	0·0000472

In calculating k, the times were expressed in minutes Calculate the heat of activation from these results.

(17) Hinshelwood and Burk found the following values for the effect of temperature on the velocity constant of the reaction

$$2N_2O = 2N_2 + O_2.$$

Temp. ° Abs.	1,125°	1,053°	1,030°	1,001°	838°
$\log_{10}(k \times 10^3)$	4·064	3·223	2·940	2·580	0·040

The times were measured in seconds, and the concentrations in gram-molecules per litre. Calculate the heat of activation for the two gram-molecules, assuming that the Arrhenius equation holds at these temperatures (see p. 371).

(18) In determining the rate of reaction of ethyl bromide and potassium hydroxide, equal quantities of N/10 solutions of the reactants were used, and 20 c.c. of the reacting liquid were withdrawn at definite times (t) from the start, and titrated with $\frac{N}{10}$ acid. The volume of acid, x, required is shown in the table:

Time t, mins.	x.
0	20·0
21	14·71
46	11·14
97	7·42
164	2·92

Calculate the order of the reaction and the value of the velocity con stant. (The data are due to Hinshelwood and Grant.)

(19) Blandon and Thompson investigated the order of the reaction between methyl iodide and pyridine. The following data were obtained :—

a and b are the concentrations in gram-molecules per litre of methyl iodide and pyridine respectively,

t is the time, in minutes,

x is the concentration, in gram-molecules per litre, of the quaternary iodide ($C_5H_5NCH_3I$) formed.

The reaction was carried out at 60° C.

$$a = 0{\cdot}03222$$
$$b = 0{\cdot}3013$$

t	57·5	89·5	135·5	182·5	228·5
$10x$	0·282	0·401	0·536	0·648	0·721

Make calculations to see whether this reaction follows the bimolecular law, and calculate the velocity constant.

CHAPTER IX

THE PHASE RULE

172. The Study of Heterogeneous Equilibria. The Phase Rule.—In the last chapter, chemical equilibrium was dealt with from the point of view of the Law of Mass Action. Whilst that treatment was primarily concerned with homogeneous equilibria, it was also shown that it could be made to apply to heterogeneous equilibria, *i.e.*, equilibria in reactions taking place between reactants in more than one phase (§ 160).

The Phase Rule provides another method of treatment of heterogeneous equilibria. The Rule, which enables the behaviour of a heterogeneous system to be forecast under various experimental conditions, was deduced by Willard Gibbs (1874–78). It was obtained by thermodynamical deductions, and does not involve any assumptions as to the nature of matter, and so is not dependent upon any hypothesis concerning matter. There are no exceptions to the rule, if it is applied properly. Gibbs' treatment was highly mathematical, and his paper was published in an American journal which was not very widely read, with the result that the Phase Rule was not known and accepted for some time. It was owing to its adoption by Roozeboom, van't Hoff, and Ostwald, and the examples they brought forward of its application, that it became generally known. The Phase Rule co-ordinated a number of phenomena under one law, and by its use the behaviour of previously untested systems could be forecast.

173. The Terms Involved.—The Phase Rule is stated in terms of the number of *phases* present in a system at equilibrium, the number of *components* of which the system may be made up, and the number of *degrees of freedom* which may be altered without causing an alteration in the number of phases. It is difficult to put the Rule into words, and for that reason it is best expressed mathematically by the equation

$$P + F = C + 2,$$

where P is the number of phases, C the number of components, and F the number of degrees of freedom.

It must be pointed out that the Rule only applies when equilibrium has been attained. There must be such a quantity of each phase present that when more is added the equilibrium is not altered.

It is now necessary to obtain some idea of what these terms mean. It must be emphasised that for a proper understanding of, and capacity to apply, the Phase Rule, the meaning of the terms involved must be perfectly understood.

Phase.—A phase may be defined as any part of a system which is homogeneous throughout, and is separated by a bounding surface from other homogeneous parts of the system.

Consider ice, water, and water vapour. These are three phases of the same substance, water, and all three can exist together, as will be shown later. It is usual, however, for only two to exist side by side. Thus, if a beaker of water were to be placed in a vessel which could be evacuated, the number of phases present after evacuation (and before, for that matter, see below) is two—water, and water vapour. Consider a saturated solution of common salt, with excess of solid salt remaining over, under similar circumstances. Here the number of phases is three—the solid salt, the salt solution, and the water vapour. Each phase must, of course, be in one of the states, solid, liquid or gas. In the gaseous state there can only be one phase, no matter how many different molecular species make it up, since gases are always completely miscible. A gas mixture is always homogeneous, and thus falls within the definition of a phase. Thus, when we have a beaker of water exposed to the air, there are still only two phases present—a liquid phase, the water, and a gaseous phase, water vapour and air.

Liquids may, or may not, form a single phase. It depends on their miscibility. If a liquid is immiscible with another there will be two phases. If it is partly miscible there may be one phase, or there may be two, depending upon the concentration.

Solids are invariably regarded as separate phases, except in the instance of a solid solution. Otherwise, even though the mixture be made very intimate, the number of separate molecular species present gives the number of phases. Thus, many forms of sulphur can exist together; these are all separate phases.

It must be carefully borne in mind that the Phase Rule itself has nothing whatever to do with the amounts of the different phases present (apart from the fact that there must be sufficient of the phases to give equilibrium), but merely their number.

Components.—The number of components in a system is the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.[1]

It is rather more difficult to grasp the meaning of the term

[1] Findlay "The Phase Rule and its Applications" (Longmans), p. 8.

"component" than it is that of "phase," but some examples will make the matter clearer.

Consider an equilibrium system containing sodium sulphate and water. Such a system could include various phases—water, vapour, ice, various hydrates of sodium sulphate; but the composition of each phase can be expressed by chemical equations which involve only anhydrous sodium sulphate and water. Consider three of the possible phases—$Na_2SO_4.10H_2O$, Na_2SO_4, and solution. Then

$$\begin{aligned} Na_2SO_4.10H_2O &= 1Na_2SO_4 + 10H_2O, \\ Na_2SO_4 &= 1Na_2SO_4 + 0H_2O, \\ \text{Solution} &= xNa_2SO_4 + yH_2O. \end{aligned}$$

The *smallest* number of independently variable constituents by which the composition of the phases present at equilibrium can be expressed is two—Na_2SO_4 and H_2O. This is referred to as a two-component system.

In the dissociation of calcium carbonate by heat, there are three different molecular species, but the composition of each phase can be expressed in terms of any two of the molecular species. Thus, the possible phases present at equilibrium are calcium carbonate, $CaCO_3$, calcium oxide, CaO, and carbon dioxide, CO_2. If any two of the constituents are chosen, the composition of all the phases is determined. Take, for example, CaO and CO_2 for the two constituents; then,

Phase.

$$\begin{aligned} CaO &= CaO + 0\ CO_2, \\ CO_2 &= 0\ CaO + CO_2, \\ CaCO_3 &= CaO + CO_2. \end{aligned}$$

If, now, $CaCO_3$ and CO_2 are chosen for the two constituents,

Phase.

$$\begin{aligned} CaO &= CaCO_3 - CO_2, \\ CO_2 &= 0\ CaCO_3 + CO_2, \\ CaCO_3 &= CaCO_3 + 0\ CO_2. \end{aligned}$$

In both examples, the smallest number of constituents which fix the composition of the phases present at equilibrium is two, and this again is a two-component system.

In the system—sulphur and its allotropes, liquid sulphur, and sulphur vapour—the compositions of all the phases can be expressed in terms of one constituent, sulphur, and this is therefore a system of one component.

Degree of Freedom.—The number of degrees of freedom of a system is the number of factors, temperature, pressure, and concentration of the components, which may be varied without altering the number of phases present.

Pressure, temperature, and concentration are the only variables concerned in the definition of "degree of freedom" (for all ordinary purposes). Any particular phase may be able to exist under different conditions of these variables, but other variables will not enter into the question. Thus, the electrical condition of the system might be altered, but such a variable is not regarded as a "degree of freedom" from the Phase Rule point of view, because it has no specific action on the course of chemical change. It is usual, in Phase Rule deductions, to regard capillary forces as negligible. Otherwise, an extra degree of freedom, the surface tension (or interfacial tension), would have to be introduced, for it is known that variation in this may influence the course of a chemical change, owing to difference in concentration of the substance in the surface layers (§ 343).

Suppose there is a gaseous phase only. It is known that the product of the pressure of the gas and its volume is constant, if the temperature is constant. If, then, the temperature and the pressure are fixed, the volume of the gas is fixed, and the system is completely defined. In other words, if the temperature and pressure of a gas are given, the volume (and hence the concentration, since volume fixes it) must follow. Thus, it is necessary to fix only two of these variable factors in order completely to define the state of the system, or two may be varied without altering the number of phases present. The system therefore has two degrees of freedom.

Consider now a system made up of water in contact with its vapour. The vapour pressure will depend on temperature, but has nothing to do with the amount of water present. Hence, on fixing the temperature, the vapour pressure is fixed, and conversely. This, then, is a system with one degree of freedom.

174. Application of the Phase Rule to Systems of One Component.—Having defined the terms involved in the statement of the Phase Rule, we can now proceed to study a few systems by its aid.

The Water Vapour—Water—Ice Equilibrium.—In this system there is only one component, but the number of phases may be varied. If three phases—ice, water, and vapour—exist together, we have $P = 3$, $C = 1$, and the Phase Rule,

$$P + F = C + 2,$$

gives the result $F = 0$.

The system, therefore, has no degrees of freedom, and is called a "non-variant" (or "invariant") system. What does it mean for a system to have no degree of freedom? Turning to the definition of degrees of freedom, it is seen that it means that none of the variables, pressure, temperature, or concentration, can be varied without one of the phases disappearing from the system. Thus, the three

phases can only exist together under one condition of temperature and pressure. At the point of co-existence the temperature is + 0·0075° C. and the pressure 4 mm.

If only two phases exist together, say ice and water, or ice and vapour, or water and vapour, the system now has one degree of freedom, and is said to be univariant. This means that one of the degrees of freedom, say temperature, may be varied without causing any alteration in the number of phases.

These facts, obtained by a consideration of the Phase Rule, may be tested by experiment. The equilibrium between water and its vapour may be represented by its vapour pressure curve, which tells

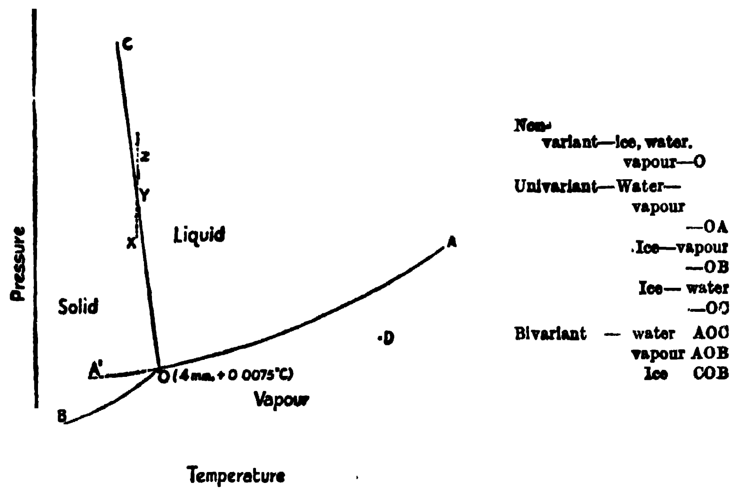


FIG. 106.—The *p-t* Diagram for Water (not drawn to scale).

the pressure of vapour in equilibrium with water at any given temperature. This curve is the curve OA in the diagram (Fig. 106). The equilibrium between ice and vapour is similarly the vapour pressure curve of ice, and is represented by OB. The equilibrium between water and ice is expressed by the effect of pressure on the freezing point of water. Obviously the curve showing the relationship between freezing point and pressure represents the equilibrium between solid and liquid water. This is OC. It is found by experiment that these curves meet in a point O. This is called the triple point, and is obviously the point where ice, water and vapour can co-exist. Note that it is a *point*, showing that there is only one set of conditions under which it is possible for the three phases to exist together, as predicted by the Phase Rule.

The lines in this diagram represent the equilibrium conditions between two phases, and express the fact that one variable can be altered without losing a phase. Returning to the triple point, it is seen that once the conditions are moved away from that point, one phase disappears. Which one it is depends upon the direction in which we move away from the point. *Anywhere* along any of the lines, however, two phases are in equilibrium. In any of the areas bounded by the lines, one phase only is present. Thus in the area AOC liquid water only is the stable phase. In AOB water vapour only is the stable phase. If it were possible to have water at a temperature and pressure represented by the point D, it would be metastable, and once set off it would all turn into vapour. It is thus seen that in a diagram of this kind a point represents the existence of an invariant system, a line a univariant system and an area a bivariant system. Thus, provided we keep in the area AOB, we can have vapour at any temperature and pressure. By altering one of the variables we do not alter the number of phases. It is possible to supercool water, and thus to continue its vapour pressure curve to A′, but the dotted line represents a metastable state.

The curve OA ends abruptly at a point, corresponding to the critical temperature (374° C.) and pressure (217·5 atm.) of water (§ 83), beyond which there can be no distinction of the gaseous and liquid phases. The curve OB will end at 0° Abs., and zero pressure, whilst no limit can be fixed to OC.

The slope of the curve OC shows that ice melts with decrease of volume. This follows from the theorem of Le Chatelier (§ 156). According to this theorem, if the temperature is kept constant, and the pressure is increased, that change will take place which is accompanied by decrease in volume. The vertical line XYZ (Fig. 106) represents change of pressure at constant temperature. If the pressure is increased when the system is at the point Y, the temperature being kept constant, the new conditions are represented by Z, *i.e.*, liquid has been formed. Hence, the melting of ice is accompanied by decrease in volume. Had the curve OC sloped the other way, Le Chatelier's theorem would have indicated an increase in volume on melting.

The diagram for water shown in Fig. 106 is not drawn to scale. Actually, the pressure differences for temperatures in the neighbourhood of the triple point O are minute. An accurate diagram for this part of the system is shown in Fig. 107, when the exaggeration in the scale of Fig. 106, just referred to, will be apparent. Also, the diagram (Fig. 106) has been very much simplified, no account being taken of the various forms of ice (no less than six), which exist at high pressures.

175. The Sulphur System.—The vapour pressure curves of the allotropes of sulphur have already been considered in connection with the study of allotropy (§ 135). The system may now be studied a little more fully. There are two solid phases which may exist permanently at equilibrium under the right conditions, the rhombic and the monoclinic forms of the element; also a liquid phase and a vapour phase. There are other solid phases capable of existence, but they are metastable, and are omitted from the present discussion. Liquid sulphur is probably colloidal in nature

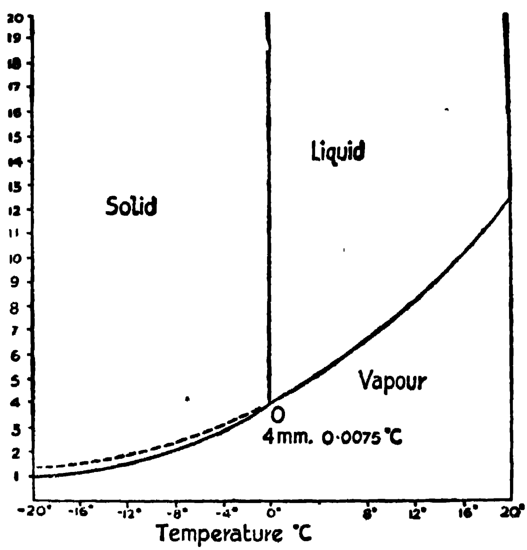


FIG. 107.—*p-t* Diagram for Water in the neighbourhood of the Triple Point.

above about 160° C. (§ 139), and may therefore itself consist of two phases. This complication is also neglected in what follows. Consider now the four phases—rhombic, monoclinic, liquid sulphur, and sulphur vapour. Can all four exist in equilibrium? In this case there would be four phases, one component, and substituting in the Phase Rule equation

$$P + F = C + 2,$$

we should get $F = -1$. This is, of course, impossible; and so for a system consisting of a single component it is not possible to have four phases at equilibrium together.

It will be possible to have three or any less number of phases together, for then the conditions are similar to those holding for the water system. Thus, the three phases, monoclinic, liquid and

vapour, could co-exist at a point, for the system would be invariant. The three phases, rhombic, liquid, and vapour, could theoretically exist together, but this can only occur in the metastable state. Two phases could exist along a line in the diagram, and one phase in an area. The vapour pressure-temperature curve is given in Fig. 108.

OB is the vapour pressure curve of rhombic sulphur, OA the

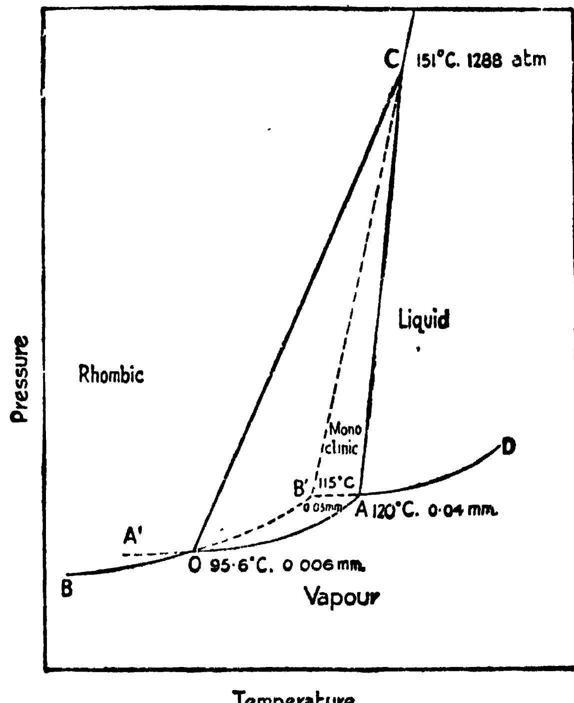


FIG. 108.—*p-t* Diagram for the Sulphur System (not drawn to scale).

vapour pressure curve of monoclinic sulphur, and AD that of the liquid. OC represents the equilibrium between monoclinic and rhombic sulphur, and is derived from the effect of pressure on the transition point. AC is the equilibrium curve between monoclinic sulphur and liquid sulphur, *i.e.*, the effect of pressure on the melting point of monoclinic sulphur. It will be noticed from the diagram that the curve representing the equilibrium between rhombic and monoclinic sulphur, OC, slopes away from the vertical, to the right; as already stated, this line represents the effect of pressure on the

transition point between the two forms, and it is clear that the transition point is raised by the application of pressure. By the theorem of Le Chatelier (§ 156), it follows that monoclinic sulphur is formed from rhombic with increase in volume. The curve AC also slopes away from the pressure axis very slightly, and so transition from liquid to monoclinic sulphur is accompanied by decrease in volume.

At the point O there are three phases in equilibrium—rhombic, monoclinic and vapour, and if one of the variables is altered one of the phases disappears. Similarly, A is also a triple point between monoclinic, vapour, and liquid. The same remarks apply as to

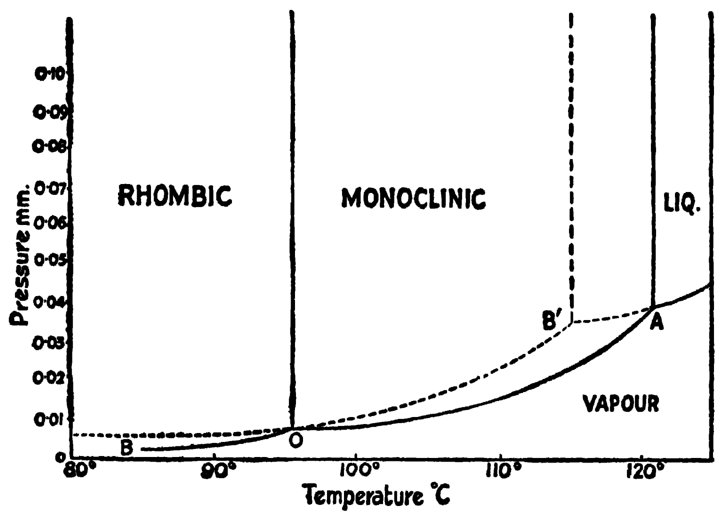


FIG. 109.—*p-t* Diagram for Sulphur in the neighbourhood of the Triple Points.

variation of one of the degrees of freedom. It is possible to supercool liquid sulphur down to the point B′, and it is also possible to heat rhombic sulphur above the transition point along OB′. This is because the change from the one form to the other is comparatively slow. The line B′C represents the equilibrium between rhombic and liquid sulphur. The point B′ is thus another triple point, but it is a metastable one, and is not frequently attained. The lines in the curve represent the equilibria between two phases; the areas represent the existence of single substances, which can remain by themselves under any temperature and pressure enclosed by the area. Since the curves AC and OC meet at C, for which the conditions are 151° and 1,288 atmospheres, it follows that if liquid sulphur were cooled at a pressure higher than 1,288 atmospheres,

rhombic sulphur would crystallise at once, no monoclinic being formed.

As with the water diagram, the scale of this curve is much exaggerated, and shows the area in the neighbourhood of the points O, A, etc., much enlarged compared with the rest of the diagram. An accurate diagram of the curves in the neighbourhood of 100° C. is given in Fig. 109. It should be pointed out that although the line OB has been drawn in Fig. 108 as though it had been followed experimentally throughout its entire length, the vapour pressure of rhombic sulphur is so low that the curve has not been followed below a temperature of 85° C., as indicated in Fig. 109. The reason for drawing the curve OB in Fig. 108 is to show the general shape of it. It would follow this course if the vapour pressure could be measured.

176. Systems of Two Components.—As an example of a system of two components, we may take a metallic alloy, say an alloy of zinc and cadmium. Pressure will not have very much effect on this equilibrium, so the two variables temperature and composition only need be considered. Pressure affects equilibria the more considerably, the greater the volume changes involved. The effect of pressure will therefore be greatest in gaseous systems, and least in solid systems. If the number of components in a system is two, it is possible to have four phases in equilibrium, but the system would be invariant. Thus

$$P + F = C + 2,$$

gives, when $P = 4$ and $C = 2$, $F = 0$.

Since the vapour pressures of solids are small, and experiments are usually done under atmospheric pressure, so that no gaseous phase exists, it is usual to call such a system as this a condensed system, and we can write a " reduced " phase rule

$$P + F' = C + 1,$$

the equation giving F', the number of degrees of freedom which the system can possess in addition to the pressure. It must be remembered that an assumption has been introduced here, *viz.*, that the external pressure is large compared with the vapour pressure of the components, and so the new " reduced " Phase Rule is only approximate.

The Phase Rule diagram for alloys such as those of zinc-cadmium is given in Fig. 110. In this case there is no compound formation, and no miscibility of the components in the solid state. The curve AC represents the freezing point curve of zinc to which successive small quantities of cadmium are added. The curve BC

is the freezing point curve of cadmium to which small quantities of zinc are added. C is the point at which solid zinc and solid cadmium are in equilibrium with the fused mass. At this point we have three phases, and therefore (using the reduced equation) no degrees of freedom. Hence, a *point* is found on the diagram corresponding to this condition. Along the line AC, pure zinc separates out, and is in equilibrium with the melt, so that here we have two phases only and therefore one degree of freedom, for which we should expect to have a *line* on the diagram. This is so.

The point C is called the eutectic point. If we have a fused mixture rich in zinc, and cool it, zinc will begin to separate out, and

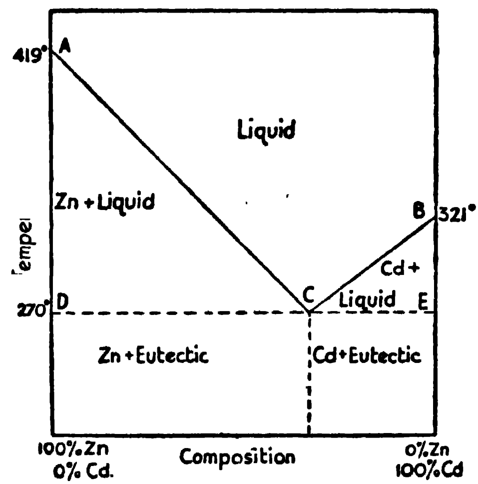


FIG. 110.—Freezing Point Diagram for Zn–Cd Alloys (simplified).

the composition of the residue will therefore be moved along the line AC until the eutectic point is reached, when the whole mass will crystallise Similar remarks apply when an alloy rich in cadmium is taken. The dotted lines in the diagram represent the boundary conditions between the separation of crystals of one of the metals and complete solidification of the mass.

Strictly speaking, the curve given in Fig. 110 is not quite accurate. A simplification of the problem has been effected in the above treatment, which leads to a slight inaccuracy. The areas marked ACD and BCE, representing the conditions under which zinc and cadmium respectively separate from the liquid alloy, are two-phase, univariant areas (since we are dealing with a condensed system, and $P + F = C + 1$). Univariant means here that if any *one* of the three variables, temperature, composition of solid phase, and com-

position of the liquid phase, is fixed, then the other two are uniquely fixed, and cannot be varied without the disappearance of one of the phases.

The diagram (Fig. 110), on the other hand, indicates that one and the same solid phase (*viz.*, pure zinc or pure cadmium) can be in equilibrium with a continuous range of liquid compositions (all along AC or BC), *i.e.*, fixing the composition of the solid phase does *not*, according to this diagram, fix the composition of the co-existing liquid phase. As shown in the previous paragraph, this is at variance with the Phase Rule.

The strictly accurate diagram is shown in Fig. 112. Here the dotted lines represented the composition of the solid phase in equilibrium with the liquid at any given temperature. These lines deviate a little from the vertical, the latter representing, of course, pure metal. In actual fact, this deviation, though theoretically necessary, may be vanishingly small, and quite unimportant for practical purposes.

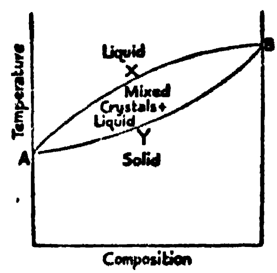


FIG. 111.—Equilibrium Curve for Mixture giving Solid Solutions.

An exactly similar case to this is the equilibrium between a salt and water. The eutectic point is here called the cryohydric point, and this case is dealt with in the next chapter (§ 212).

Where two substances form a solid solution, the matter is quite different. At most there can only be two phases present, liquid and solid solution, and therefore, from the "reduced" Phase Rule,

$$P + F' = C + 1,$$

F' must always be at least 1. Hence there can be no eutectic point, as in the previous case. One type of equilibrium diagram is shown in Fig. 111. AXB is the curve indicating the equilibrium between liquid and the mixed crystals + liquid. It is the melting point curve. AYB represents the equilibrium between mixed crystals + liquid and solid, and is the freezing point curve. For a further discussion of this system, see § 219.

There is one more possibility. One or more chemical compounds may be produced. Thus, consider the case in which the two components of the system give rise to a chemical compound of definite composition. This substance will act just as if it were a foreign substance, and the freezing point curve will show two eutectics. An example is the alloy of magnesium and tin, which form a compound Mg_2Sn. The Phase Rule diagram is given in Fig. 113.

The eutectic B is that at which the three phases Mg, Mg_2Sn, and liquid, are present. The eutectic A is that at which Mg_2Sn, Sn and liquid are present. Along BE pure magnesium will separate out, for it is the equilibrium curve between Mg and the liquid alloy. Along AD, and also DB, the pure compound will be deposited, and along CA pure tin.

The point D is at the maximum of the curve ADB, and represents the composition of the pure compound. This follows from the fact that the addition of a second substance to a pure compound lowers the melting point of the latter. The addition of either magnesium or tin to the compound Mg_2Sn will result in the lowering of its

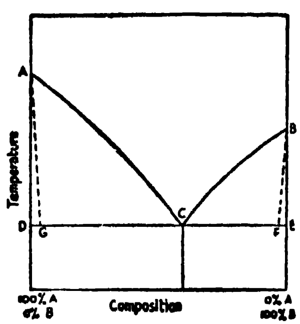


Fig. 112.—Phase Rule Diagram for Zn-Cd Alloys.

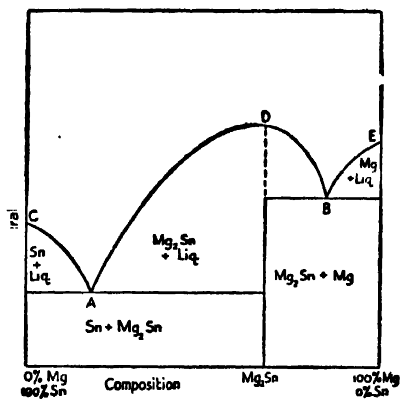


Fig. 113.—Phase Rule Diagram for Mg–Sn Alloys.

melting point. Hence, the maximum of the curve must represent the composition of the pure compound.

The existence of a hump in the freezing point composition curve indicates the existence of a compound. The number of them gives the number of compounds that can be found. The curves representing the equilibrium between salt hydrates and water (solubility curves) frequently show this behaviour. In the case of the ferric chloride-water system, there are no less than four humps in the solubility curve (Fig. 145, p. 448).

The vapour pressure curves of salt hydrates are interesting examples of the application of the Phase Rule. If some hydrated copper sulphate pentahydrate, $CuSO_4$, $5H_2O$ be placed in a tensimeter (see p. 319), together with a little of the trihydrate, $CuSO_4$, $3H_2O$, the vapour pressure of the mixture is found to remain constant so long as there is any of the pentahydrate present, but as soon as all this has gone, the vapour pressure suddenly drops until it

reaches another constant level. It remains level here until all the trihydrate has been used up, and then there is another sudden drop. Again the vapour pressure remains constant until all the salt has been completely dehydrated. The temperature is supposed to remain constant during these changes. These facts are represented on the diagram (Fig. 114), and are capable of a very simple explanation on the basis of the Phase Rule. When the pentahydrate is being dehydrated, it is at first in the presence of some trihydrate. There are, therefore, two solid phases, and three altogether, for there is also the water vapour. There are only two components in this system. Hence by the Phase Rule,

$$P + F = C + 2,$$

$P = 3$, $C = 2$, and hence $F = 1$. The system is univariant, but as the temperature is fixed, this one degree of freedom is removed. At constant temperature then the system is invariant. Hence, while there are two components, the vapour pressure must be constant. When all the pentahydrate has been converted into trihydrate, there is a sudden drop to the new dissociation pressure (§ 160), and the same conditions then apply. Treatment of this problem by the Law of Mass Action gives the same results (§ 160).

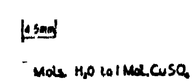


FIG. 114.—Vapour Pressure Curve of Copper Sulphate Hydrates at Constant Temperature.

The phenomenon of efflorescence is closely bound up with this. The compounds $CuSO_4.5H_2O$ and $CuSO_4.3H_2O$ can only exist together at one definite pressure of water vapour. If the vapour pressure of water in the atmosphere exceeds this amount, then all the trihydrate goes into pentahydrate; if it is less than this the pentahydrate gradually becomes transformed into the trihydrate, losing water, in making the vapour pressure of water in the atmosphere in its neighbourhood equal to the dissociation pressure. This is the phenomenon of *efflorescence*, where a hydrated salt loses its water of crystallisation and falls to a powder of some lower hydrate or the anhydrous salt.

The absorption of water by a salt, and the solution of the salt in the water absorbed is called *deliquescence*. A solid will deliquesce in moist air if the pressure of water vapour surrounding it is greater than the vapour pressure of its saturated solution. All salts would deliquesce if the vapour pressure of the water in the atmosphere were sufficiently great, but as it seldom exceeds 15 mm., and there

are few salts with saturated solutions of vapour pressure lower than this, few salts actually do show this phenomenon. The vapour pressure of a saturated solution of calcium chloride is only 7·5 mm. at 20°, and so the salt is deliquescent. That of copper sulphate is 16·0 mm., and so this salt rarely deliquesces.

Many applications of the Phase Rule to two component systems are mentioned in Chapter X.

177. Systems of Three Components.—As the number of components in a system is increased the consideration of it becomes more difficult. As examples of the systems which fall into this class there are systems consisting of water and two salts with a common ion, such as $KBr + NaBr + H_2O$, $NH_4NO_3 + AgNO_3 + H_2O$, and $NaCl + Na_2CO_3 + H_2O$. If new compounds are formed in a system of this type, they can only have a composition between that of two of the three components (double salts and hydrates), and thus any phase which may occur can have its composition expressed in terms of the three components. A system consisting of water and two salts without a common ion would not come into this class, since new phases might be produced by double decomposition, of which the composition could not be expressed in terms of three of the components. This would be a four-component system. If water were absent, the two salts without a common ion would form a three-component system. Another example of a three-component system is the case of a salt and water where the salt undergoes hydrolysis, *e.g.*, bismuth nitrate.

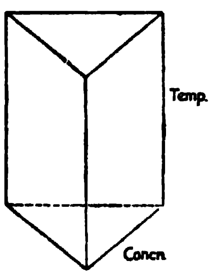


FIG. 115.—Co-ordinates for Representation of a Three-component System.

For a given number of coexisting phases, the number of degrees of freedom in a system of three components is one greater than in a system of two components. For three components, $P + F = C + 2 = 5$. The maximum number of phases is, therefore, 5, when the system is invariant ($F = 0$); and the maximum number of degrees of freedom is 4, when $P = 1$ (one gaseous phase only). When $F = 4$, the temperature, pressure and concentrations of two of the components in the single gaseous phase may be varied arbitrarily, within certain limits.

178. Graphical Representation of Systems of Three Components.—It is not always possible to represent the data for a ternary system graphically. Very often, however, condensed systems are dealt with in which the pressure may be regarded as constant, and this simplifies matters a little. It is clear that if we have to represent

the remaining three variables, temperature and two concentrations, in a diagram, it will have to be a space diagram. This can be done by representing the composition by triangular co-ordinates, and the temperature at right angles to the composition diagram. This is shown in Fig. 115.

If the temperature is constant, the curve can be represented in a plane, being a section of the prism at the right temperature. Such diagrams are called *isothermal diagrams*, and the whole solid prism can be built up by the superposition of the isothermal diagrams. This is a good method for constructing the solid models which are required to follow these systems.

The base of the prism is taken as an equilateral triangle. The composition of each pure component is represented by a vertex. The length of the side is divided into a hundred parts. The composition of a ternary mixture is obtained by determining the distance of the point from a side measured parallel to the sides of the triangle. This method of representation is due to Roozeboom. To represent a mixture consisting of *a*, *b*, and *c* per cent. of the components A, B, and C respectively, one side of the triangle is divided off into a hundred parts, and a portion Bx is measured off to represent *a* (Fig. 116). An amount Ay is now measured off to represent *b*. Then the remainder, xy, must be the amount of C, as altogether the compositions must add up to 100. Through x and y lines are drawn parallel to the sides of the triangle. The point of intersection Z, is the point representing the composition of the ternary mixture. The distance of Z from the sides, measured along lines drawn parallel to the sides, obviously, from the geometry of the figure, gives the composition *a*, *b*, and *c*.

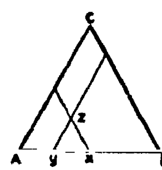


FIG. 116.

Other methods of representation have been adopted. That due to Gibbs represents the composition of the mixture by perpendicular distances of a point on the diagram from the sides.

If it is necessary to show the effect of temperature, this can only be done with a solid model, the temperature axis being vertical.

The use of triangular diagrams is shown in the study of the mutual solubility of three liquids, such as benzene, water, and acetic acid. This experiment is described on p. 403.

If the compositions of two phases are represented by the points X and Y, within the triangle, then a point P on the line joining X and Y, represents a phase consisting of a mixture of X and Y in the proportions PY to PX (Fig. 117). It follows that if the point representing the composition of a phase Z (Fig. 118) is joined to the point A, representing the pure component A, then any point R on

this line represents a phase which is a mixture of A and Z in certain proportions (RZ : RA). This fact is often employed in studying saturated solutions. If the point Z in Fig. 118, represents the composition of a saturated solution, and some of the solid remaining over at the bottom of the solution is removed and analysed whilst still moist with the mother liquor, its composition will be indicated by some point such as R. The line ZR produced will cut one of the sides at some point. This point represents the composition of the solid in equilibrium with the saturated solution. It is often one of the pure components, as in the diagram we have chosen, but it need not be. In the latter case, the formation of a double-salt would be indicated. Lines such as ZR are called *tie-lines*. The analysis of a number of mixtures similar to the above give tie lines intersecting at the composition of the solid phase in equilibrium with the solution.

As one of the simplest examples of the application of the above principles, the system ammonium sulphate—ammonium chloride—

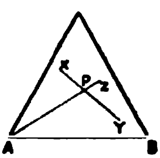


FIG. 117.

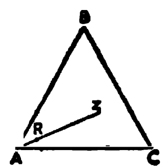


FIG. 118.

water, may be taken. It is a ternary system, since it is made up of two salts with a common ion (the ammonium ion) and water. The object is to discover whether any double-salt is formed between these two constituents. In the diagram (Fig. 119), A represents ammonium chloride, B ammonium sulphate, and C water, and it is drawn for a certain specified temperature, say 25° C. If a saturated solution of ammonium chloride is taken, its composition will be represented by a point P on AC. If, now, ammonium chloride is shaken up with ammonium sulphate solution, the composition of the saturated solution will be represented by a point, Q, inside the triangle, since it will now contain all three constituents. If the experiment is repeated with other solutions of ammonium sulphate of different concentrations, further points inside the triangle will be obtained, which all lie on the line PQR. If the damp solids as filtered from the various saturated solutions are analysed, and their compositions plotted on the triangle, it is found that the tie-lines intersect at A, showing that the solid in equilibrium with the solutions so far considered is ammonium chloride. If, now, a saturated solution of ammonium sulphate in water is analysed, its

composition may be represented by X, on BC. If ammonium sulphate is shaken up with ammonium chloride solution, and the saturated solution is analysed, its composition may be represented by a point Y. By repeating the work with ammonium chloride solutions of various concentrations, the curve RYX is obtained. Analysis of the damp solids in contact with the different saturated solutions, shows that their compositions may be represented by points on tie-lines joining the curve RYX to B. Thus the solid in equilibrium with the saturated solutions just considered is ammonium sulphate. If the tie-lines ending at R are drawn, it is

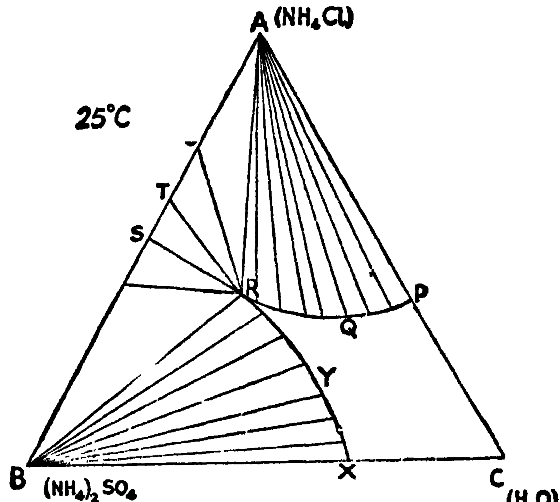


FIG. 119.—System $NH_4Cl - (NH_4)_2SO_4 - H_2O$ (The diagram is schematic only, and is not drawn to scale.)

found that they cut the side AB at various points A, U, T, S, B, etc. This means that the solid in equilibrium with the saturated solution represented by R is variable in composition, over the whole range $x\ NH_4Cl$, $y\ (NH_4)_2SO_4$. There is no double-salt formation.

The interpretation of the diagram according to the Phase Rule may now be considered. There are three components—the two salts, and water at the point R, if both the salts are taken in sufficient quantity to saturate the solution. The number of phases is three—one liquid, and two solid. In a condensed system,

$$P + F' = C + 1,$$

hence, in this case, $F' = 1$. The diagram, however, is an isothermal one, so that temperature, the one remaining variable, is fixed, and the point *on the diagram* is invariant. It is called an

isothermally invariant point. It must be emphasised that in a three-dimensional model the point would not be invariant. The interpretation of this is, that at the temperature for which the diagram is drawn, the solution of composition R is the only one that can exist, in a stable state, in contact with both ammonium chloride and ammonium sulphate. If there is insufficient of one of these (say ammonium chloride) to saturate the solution, there are now only two phases—one liquid, and one solid (ammonium sulphate), whilst the number of components remains the same. The system is now actually bivariant, but, since temperature is fixed in the isothermal diagram, it is effectively univariant, as far as we are

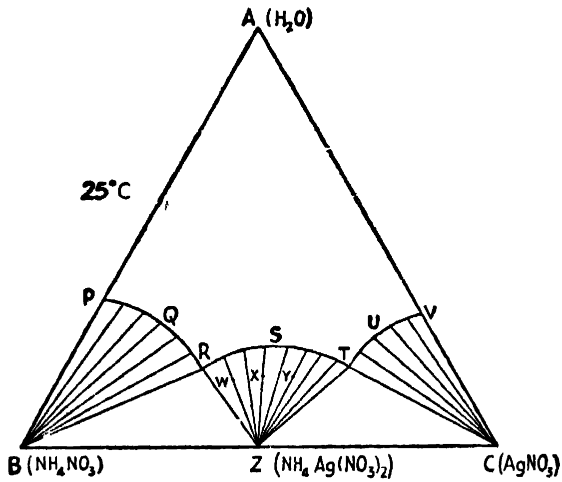


FIG. 120.—System $NH_4NO_3 - AgNO_3 - H_2O$ (schematic only).

concerned, and the equilibrium is now represented by the line RX. In the complete model, where temperature is represented by a vertical axis, the point R, and others like it, would lie on a line (the system being univariant), and the lines RP and RX would lie on surfaces (the system being bivariant).

The above is a very simple case, in so far as there is no formation of a double-salt. In a system such as that of ammonium nitrate-silver nitrate-water, there is formation of a double-salt, the composition of which may be obtained from the diagram.

Let A (Fig. 120) represent water, B ammonium nitrate, and C silver nitrate. The point P represents a saturated solution of ammonium nitrate in water. If, now, ammonium nitrate is shaken up with a dilute solution of silver nitrate, the composition of the saturated solution is now represented by Q. Repetition of the

experiment leads to points on the curve PQR. Analysis of the moist solids in contact with the various saturated solutions gives points on tie-lines connecting the curve PQR with B, showing that the solid in equilibrium with these solutions is ammonium nitrate. If, now, the addition of silver nitrate is continued, the composition of the saturated solution is now found to lie on the line RST. The compositions of the moist solids in contact with these saturated solutions are represented by points, such as W, X, Y, which when joined up with the points representing the compositions of the saturated solutions themselves, and produced backwards, cut the BC axis at Z, which is found to correspond to the double-salt

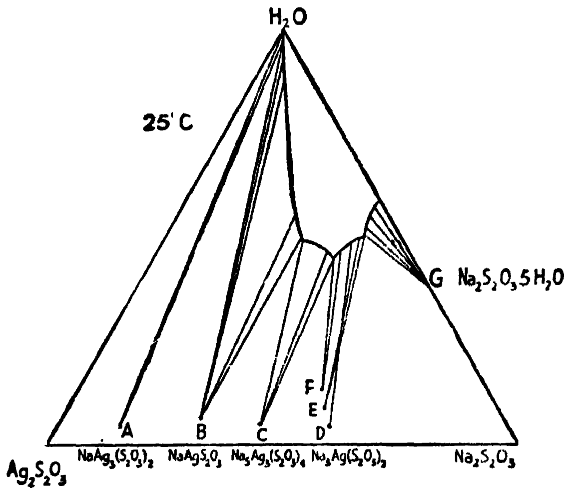


FIG. 121.—System $Na_2S_2O_3 - Ag_2S_2O_3 - H_2O$ at 25° C. (After Bassett and Lemon.)

$NH_4.Ag.(NO_3)_2$. This salt, then, is the substance in equilibrium with saturated solutions over the composition range RST. If a saturated solution of silver nitrate is taken, its composition is represented by V. If silver nitrate is shaken up with ammonium nitrate solution, saturated solutions, the compositions of which are represented by points on the line TUV, are obtained. The solid in equilibrium with these solutions is silver nitrate. The two points R and T are invariant in the isothermal diagram, but actually represent univariant systems, as previously explained.

If the tie-lines happen to intersect at a point inside the triangle, the point of intersection still represents the composition of the solid in equilibrium with the saturated solution. This occurs when a hydrated double-salt is formed.

The triangular diagram may frequently be very complicated. As an example of the information that can be derived from these studies, the system $Na_2S_2O_3 - Ag_2S_2O_3 - H_2O$ may be quoted. It has recently been investigated by Bassett and Lemon (*J. C. S.*, 1933, 1423–1427). The student who wishes to carry his work further is recommended to consult the original paper. A very much simplified diagram only can be given here. The form of the diagram is shown in Fig. 121.

The points A, B, C, D, E, F, G are found to represent the following salts :—

A. $NaAg_3(S_2O_3)_2 . H_2O$.
B. $NaAgS_2O_3 . H_2O$.
C. $Na_5Ag_3(S_2O_3)_4 . 2H_2O$.
D. $Na_3Ag(S_2O_3)_2 . H_2O$.
E. $Na_3Ag(S_2O_3)_2 . 2H_2O$.
F. $Na_5Ag(S_2O_3)_3 . 3H_2O$.
G. $Na_2S_2O_3 . 5H_2O$.

All these salts are, therefore, capable of existence. In all cases, except the last, it is to be noted that the tie-lines intersect within the triangle, showing that the double-salts are hydrated.

There are many other facts that can be derived from a study of these triangular diagrams, and the student who is interested should consult one of the monographs devoted to the Phase Rule (see list at end of chapter).

SUMMARY

The Phase Rule provides a means of studying heterogeneous equilibria. It states that, in a system at equilibrium,

$$P + F = C + 2,$$

where P is the number of phases, F the number of degrees of freedom, and C the number of components.

A *phase* is any part of a system which is homogeneous throughout, and is separated by a bounding surface from other homogeneous parts of the system.

The number of *components* in a system is the smallest number of independently variable constituents, by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.

The number of *degrees of freedom* is the number of variable factors, temperature, pressure, and concentration of the components, which must be fixed in order that the condition of the system may be completely defined.

A system possessing no degrees of freedom is said to be invariant, one possessing one degree of freedom is univariant, etc.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 22.—To determine the transition point between rhombic and monoclinic sulphur.

Although the experimental methods of determining transition point are given in Chapter VII., the actual work is best carried out here, as it is a Phase Rule problem.

The simplest method is the dilatometric method, and the simple dilatometer described by Sherwood Taylor ("Elementary Practical Physical Chemistry," p. 76) may be conveniently employed. It is made by connecting a test-tube with a fairly long capillary tube which has been bent at right angles as shown in the diagram.

Boil some sulphuric acid (1 to 3) to free it from air. Powder some roll sulphur, and put it in the tube (about two-thirds of the tube should be full). Add some of the sulphuric acid, and warm to get rid of air. Pour off most of the acid, and fill with fresh "boiled-out" acid. Insert the cork and capillary tube and arrange that the thread of acid is at the zero of the scale, or thereabouts, when placed in some calcium chloride solution warmed to about 80° C. in a beaker.

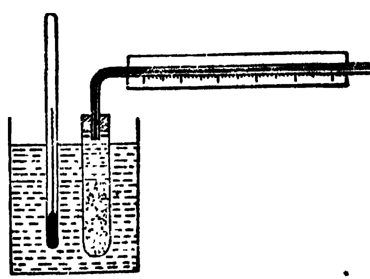


FIG. 122.—Dilatometer.

Warm the solution slowly on a sand bath, note the temperature at intervals, and the position of the thread of acid. When the transition takes place the expansion is greater. Plot the increase in volume per half degree rise in temperature and determine the transition point. (Theory, p. 316.)

Experiment 23.—To determine the dissociation pressure of copper sulphate hydrates.

Obtain a tensimeter and place in one of the bulbs, copper sulphate pentahydrate which has been allowed to stand for a short time in a desiccator. This ensures that a small amount of trihydrate will be present. Carry out the experiment as described on p. 317.

Experiment 24.—To study the mutual solubility of benzene, water and acetic acid.

Have two burettes, one filled with water, and the other with glacial acetic acid. Put 5 c.c. of benzene in a conical flask provided with a cork, add 1 c.c. of water, and run in glacial acetic acid until a clear solution is obtained on shaking. Note the volume required. This gives one composition for the mutual solubility. Add another 2 c.c. of water to the mixture, and then add more acetic acid until on shaking the solution is clear. Repeat with other concentrations. Plot the data on a triangular diagram. Since these experiments are carried out at constant temperature, the isothermal diagram is all that is required. (Theory, p. 396.)

SUGGESTED FURTHER PRACTICAL WORK

(1) Determine the freezing point curve for lead-tin alloys. (See Sherwood Taylor, "Elementary Practical Physical Chemistry," p. 87.)

(2) Repetition of the study of a system such as $Pb(NO_3)_2$ – KNO_3 – $NaNO_3$ (*J. C. S.*, 1932, 2586), or some other mentioned in the scientific literature.

SUGGESTED FURTHER READING

FINDLAY, A. "The Phase Rule and its Applications." (*Longmans*, 1927.)
RIVETT, A. C. D. "Phase Rule." (*Oxford University Press*, 1923.)
RHODES, J. E. W. "Phase Rule Studies." (*Oxford University Press*, 1933.)

QUESTIONS

(1) What do you understand by the terms "phase," "component," "degree of freedom," "equilibrium"? What is the Phase Rule? Give one example of its application.

(2) What is the explanation of efflorescence and deliquescence?

(3) What do you mean by a triple point? What triple points are to be observed in the sulphur system?

(4) Draw a sketch and explain the principal features of the freezing point diagram for a mixture of two metals which do not form solid solutions. How is the diagram modified if a chemical compound is formed?

(5) How may the Phase Rule be applied to a double salt and its solution in water? What type of diagram would you expect?

(6) From the diagram for sulphur given on p. 389, answer the following questions: (*a*) is monoclinic sulphur more dense than rhombic sulphur? (*b*) is rhombic sulphur more dense than liquid sulphur? (*c*) is monoclinic sulphur more dense than liquid sulphur? Give reasons.

CHAPTER X

SOLUTIONS

179. Definition of Solution.—*A solution is a perfectly homogeneous mixture.*

Solutions of all kinds may be made. Thus, solutions of gases in gases, of gases in liquids, of gases in solids, of liquids in liquids, of solids in liquids, of solids in solids, can be prepared. Each of these classes presents numerous points of interest.

A. SOLUTIONS OF GASES IN GASES

180. Application of the Phase Rule.—All gases which do not combine chemically will mix in all proportions. If a drop of bromine is placed in a large flask, the bromine vapour rises, and fills the whole vessel. In spite of the fact that it is many times heavier than air, it forms a perfect solution with air, owing to the process of diffusion.

A mixture of two gases is a system of two components, but with only one phase. Hence, according to the phase rule

$$P + F = C + 2$$

$F = 3$. The system has three degrees of freedom. This means that the temperature, concentration, and pressure can all be varied over a limited range without the risk of any new phase appearing. It must be borne in mind however, that if these variations are made sufficiently large, there is a possibility of obtaining a new phase, for one of the gases may liquefy, if the pressure and temperature are altered in the right directions, and by sufficient amounts.

181. Dalton's Law of Partial Pressures.—The pressures of gases in solutions of gases in gases are measures of their concentrations. Indeed the usual method of measuring the concentration of a gas is by means of its pressure. A simple rule was put forward by Dalton in 1802 to express the pressure relationships in gaseous mixtures. It is known as Dalton's Law of Partial Pressures, and states that *the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.*

The pressure that each gas would exert by itself is called its partial pressure.

This law, like all the other gas laws, is only true for perfect gases, and of course it only applies where there is no chemical combination between the gases.

There is another way of stating the law. If the gases are perfect they will obey Boyle's Law, and the volumes will be inversely proportional to the pressures. We can therefore state that—*the volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the same conditions of temperature and pressure.*

This is sometimes known as the Law of Additive Volumes.

182. Determination of the Partial Pressures of Gases in a Mixture.—To test Dalton's Law all that would be necessary would be to mix two gases at known pressures and find the total pressure. If, however, we are already given a gaseous mixture and told to find the partial pressure of any gas in it, this is a more difficult matter. If a membrane can be found that will allow one gas to get through, and not the other, it is possible to carry out this experiment. Heated palladium is permeable to hydrogen, but not to any other gas, and hence the following apparatus, devised by Ramsay, can be used for determining the partial pressure of hydrogen in any mixture.

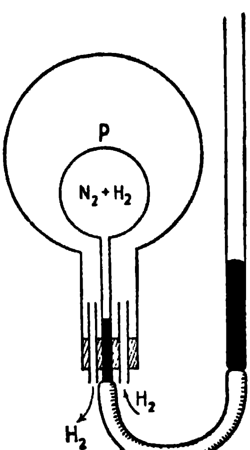


FIG. 123.—Experiment to illustrate Partial Pressures.

The palladium vessel, P, is capable of being heated, and is connected to a manometer. A mixture of, say, hydrogen and nitrogen, of which the partial pressures are required, is placed in the bulb, and a stream of hydrogen is passed through the outer vessel, at atmospheric pressure. When the palladium bulb is heated, it becomes permeable to hydrogen, and the pressure of hydrogen becomes the same inside and outside the vessel, *i.e.*, equal to one atmosphere. The pressure indicated by the manometer will, however, be greater than one atmosphere, by the partial pressure of the nitrogen inside. By taking the reading of the manometer the partial pressure of the nitrogen can be obtained, and if the original pressure of the mixture were known, the partial pressure of the hydrogen originally present could be found by difference.

This experiment in itself is not of great importance, but it illus-

trates a method of determining partial pressures, and is very similar to experiments on osmosis in which a semi-permeable membrane is used (p. 467).

An experiment to determine the partial pressure of oxygen in air may be carried out with the apparatus described below.

The vessel A, which has a capacity of about 100 c.c., is fitted with a spiral of iron wire which can be heated electrically. It is connected by means of the two-way tap C with a manometer, B. The vessel A is first exhausted by connecting the tube D to a pump and turning the tap C. Pure dry air is then allowed to pass into the bulb, which is cooled in a freezing mixture to 0° C. The tap is then turned so that the manometer is connected to the bulb, and the mercury is brought up to the mark, by raising the other limb of the manometer. The pressure of the gas is noted. The closed limb is now lowered, and the iron spiral heated. The iron combines with the oxygen, forming ferroso-ferric oxide. After a time, the current is stopped, the air in the vessel again brought to 0° C., and the mercury brought back to the mark. The difference in pressure is noted. If the initial pressure was P, and the final pressure, p, the partial pressure of the oxygen was $P - p$.

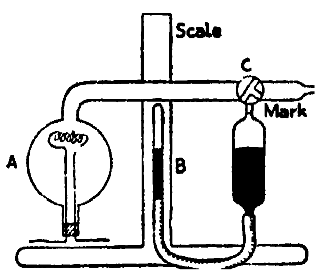


FIG. 124.—Apparatus for finding Partial Pressure of Oxygen in Air.

Where possible, it is very much easier to make use of the Law of Additive Volumes and calculate from that the partial pressure of any gas in a mixture. Thus, if a mixture of carbon dioxide and nitrogen is given, the carbon dioxide may be absorbed with caustic potash, and the decrease in volume noted.

183. Solubility of Vapours in Gases.—When a liquid A is very soluble in a liquid B, it is always found that B is very soluble in A. It is of interest to know whether a gaseous system of two components shows a similar mutual solubility between the components in each phase. Ammonia is very soluble in water. Will it attract water into the vapour phase? There is obviously an attraction between ammonia and water in the liquid state. Is there also an attraction between the two substances in the gaseous state?

There is no record of a liquid being more volatile in the presence of a gas than when it exists alone. If such a change in volatility could be found, the problem would be solved. There is, however, an obvious solution to the question. If the pressures of the two

gases are determined before mixing; and again after mixing, according to Dalton's Law, the latter pressure should be equal to the total of the initial pressures. If the final pressure is less than the sum of the original pressures, it may be concluded that there is some attraction between the molecules.

MacFarlane and Wright (*J. C. S.*, 1934, 207) investigated in this way the attraction under ordinary conditions of temperature and pressure, between the vapours of methyl alcohol, ether, acetone or chloroform, and the gases carbon dioxide, ammonia, sulphur dioxide, or hydrogen chloride. It was found that these gases show considerable attraction for the vapours of the liquids in which they are soluble, though no quantitative relationship between the attraction and solubility could be deduced.

B. SOLUTIONS OF GASES IN LIQUIDS

184. Definitions.—All gases are soluble to a greater or less extent in water. Those gases which are very soluble are invariably those which form compounds with water, *e.g.*, ammonia, or dissolve to give ions, *e.g.*, hydrogen chloride.

Several definitions of the solubility of gases in liquids have been proposed. If the volume of gas dissolved in 1 c.c. of liquid is expressed at the pressure and temperature of the experiment, the figure obtained is called the *solubility*.

The *absorption coefficient* is the volume of gas in c.c.s measured at 0° C. and 760 mm. which dissolves in 1 c.c. of water.

The absorption coefficients of gases differ very much. A table showing the absorption coefficients of a number of common gases in water is shown below :—

TABLE LXVII

Gas.	Absorption Coefficient, at 0° C.
Ammonia	1,300
Hydrogen chloride	506
Sulphur dioxide	79·8
Hydrogen Sulphide	4·68
Carbon dioxide	1·713
Ethylene	0·25
Oxygen	0·049
Nitrogen	0·024

185. Determination of the Solubility of a Gas in a Liquid.—Several methods are available for determining the solubility of a gas, depending largely upon the nature of the gas; but one method of general applicability is that devised by Ostwald, using the absorptiometer.

The apparatus consists of two parts, an ordinary gas burette, G, and a gas pipette, C. The taps T and B are three-way taps, that at R, one-way. The end of the gas pipette is dipped into air-free water, the tap turned, and the pressure so adjusted by means of the burette that the vessel C becomes completely filled with water. The taps R and B are now closed, the pipette is removed from the water, and then the volume of water it contains is measured by running off into a measuring cylinder. This gives the volume of the vessel, which volume may be called v_1. Now the pipette is filled with water as before. The tap T is turned, to put G into communication with B and F, keeping the tap B closed. By raising H, the mercury is made to fill G up to T. Now a source of the gas of which the solubility is required is connected to F. By opening T, connect F and B, but not G, and by opening B connect A and P, but not C. Gas now flows from F to B and out at P. Now shut B, and by the tap T connect G and A, and by lowering H fill G with gas. Keeping B closed, connect A and G, but not F, and allow to stand for about twenty minutes. It is advisable to have the tube A made of metal (lead or copper), as rubber is permeable to many gases, and also undergoes volume changes on twisting, etc. It is usually coiled into a spiral to facilitate shaking. Adjust H, and read the level of the mercury in G. This can be called h_1. Let the height of the barometer be p, and the absolute temperature of the pipette and burette be $T°$.

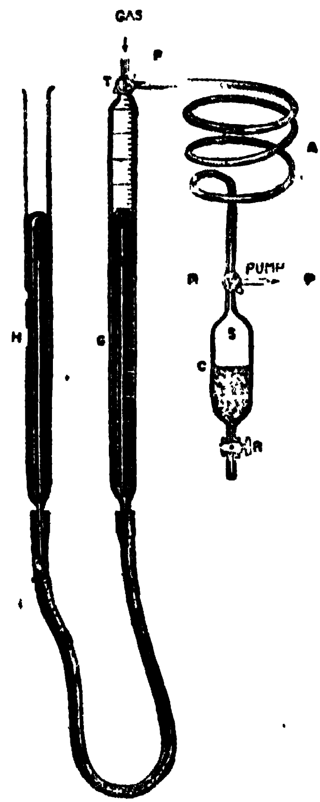


FIG. 125.—Ostwald's Absorptiometer.

Now put a measuring cylinder under C, and allow B and A to be connected, but not P, collecting the water that runs out when R is opened. If this volume is v_2 c.c., the volume remaining is $v_1 - v_2$ c.c.

B is now shut and the absorption vessel is shaken. B is opened and the burette reading taken. This process is repeated until a constant reading is obtained. Let this be h_2. The volume of gas absorbed is $h_1 - h_2 - v_2$. The volume of liquid is $v_1 - v_2$ c.c. The volume must be corrected to N.T.P. to obtain the absorption coefficient as defined above.

In this experiment it is absolutely necessary to keep the temperature of the absorption pipette constant. A slight variation may make a considerable difference to the result. It is therefore advisable to keep it in a constant temperature bath, which may or may not be at a different temperature from the gas in the burette. This temperature difference will have to be taken into account in the calculation of the result.

The absorptiometer is not a sufficiently accurate piece of apparatus for the determination of the solubility of a very soluble gas, where very small quantities of solvent would have to be used to absorb the gas contained in so small a vessel as is there available. For this purpose, an entirely different method is used, due originally to Roscoe and Bunsen.

A bulb of the shape shown in Fig. 126 is blown from thin glass, and bent as shown. The bulb should have a capacity of from 30–50 c.c. It is first weighed empty, and then it is about two-thirds filled with the solvent to be used. It is then connected to a source of the gas, the solubility of which is required, and the gas, after drying, is passed through the solvent until saturated, the bulb being kept in a constant temperature bath. The ends of the vessel are then held in a blowpipe, or Bunsen flame, and drawn off, the pieces removed being preserved. The apparatus, together with the pieces drawn off, is then weighed. The difference between the original weight of the dry bulb and the final weighing gives the weight of the saturated solution. It is now necessary to determine how much gas has been dissolved. The procedure depends upon the nature of the gas. Most very soluble gases are either acidic or basic. If the gas is basic, *e.g.*, ammonia, the vessel containing the saturated solution is placed in a dish containing a known volume of standard sulphuric acid, and is then broken by means of a glass rod. The ammonia solution neutralises some of the acid, which is then titrated with standard base. From the amount of acid used up by the ammonia, the quantity of ammonia present can be calculated, and hence its solubility. Similarly, if hydrogen chloride were the

gas under observation, the bulb would be broken under standard base, and the amount of base left over would be determined by standard acid. Or, the vessel could be broken under water, and the hydrogen chloride directly determined.

In very accurate work it would be necessary to make corrections for the weight of air displaced by the gas, and the weight of moist vapour filling the spaces in the bulb.

186. Nature of a Gas and its Solubility.—It has already been mentioned that the solubilities of gases vary enormously according to the nature of the gas and the solvent. Gases which give acidic or basic solutions, *i.e.*, solutions in which ions are formed, are much more soluble than others. Thus, we may compare the solubility of oxygen, which has an absorption coefficient of 0·049, with that of hydrogen chloride, of which the absorption coefficient is 506.

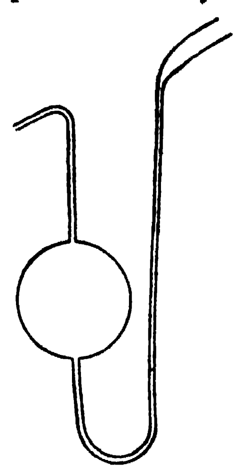


FIG. 126.—Solubility Vessel.

It is a remarkable fact that those gases which are easily liquefied are the more soluble in the usual solvents. This probably indicates miscibility of the liquefied gas with water. To illustrate this, it may be noted that alcohol vapour is soluble in water at 90° C., and the liquid alcohol itself is completely miscible with water.

The nature of the solvent is also important in deciding solubility. Thus, we may compare the solubilities of carbon monoxide and of nitrogen in various solvents. This was done by Just in 1901, and Table LXVIII embodies his results. It will be noted that the ratio of the solubilities remains practically constant, so that the solubilities increase or decrease to about the same extent in the different solvents.

These remarks, of course, would not apply to gases which dissolve in some solvents with compound formation, and in others without compound formation, *e.g.*, ammonia, which dissolves in water to form ammonium hydroxide, but in benzene without compound formation.

Work has been done on the connection between the compressibility of the solvent and the solubility of a gas in it. When gases dissolve, the solution usually occupies a greater volume than the original solvent, so that the solvent has to expand. It will do this against its compressibility, and so the tendency of the gas to dissolve is counterbalanced by the resistance of the solvent to expand. Experiments have shown that there is rough proportion-

TABLE LXVIII[1]

Solvent.	Solubilities (25° C.).		Ratio $\frac{\text{sol. CO}}{\text{sol. } N_2}$.
	N_2.	CO.	
Water	0·0163	0·0240	1·47
Aniline	0·0307	0·0536	1·75
Carbon disulphide	0·0586	0·0831	1·42
Nitrobenzene	0·0626	0·0937	1·50
Benzene	0·116	0·171	1·47
Glacial acetic acid	0·119	0·171	1·44
Toluene	0·123	0·181	1·47

ality between solubility of the gas and compressibility of the solvent.

187. Solutions of Gases in Salt Solutions.—Gases are usually less soluble in salt solutions than in pure water. Carbon dioxide, however, is more soluble in a solution of sodium phosphate, and in a solution of sodium chloride, than it is in water.

Indifferent gases, such as hydrogen, oxygen and nitrogen, are always less soluble in salt solutions, and solutions of some organic substances, than in water, the amount of diminution being the same for all gases for a given salt concentration. It is thought that the salt may combine with some of the water, forming a hydrate, and that this water is no longer available for the solution of the gas. If this is so, it should be possible to obtain valuable data as to the existence of hydrates, or of hydrated ions (p. 529), in solution from a

TABLE LXIX

Cane-sugar. Per cent.	Vol. of N_2 absorbed at 15° C. by 1,000 gms. H_2O in the solution.	Mols. H_2O per mol. sugar
0	18·83 c.c.	—
16·67	17·55 „	6·5
30·08	16·27 „	6·0
47·65	13·95 „	5·4

[1] Taken from J. Newton Friend's "Physical Chemistry," Vol. I. (Griffin). The data for several other tables in this chapter have been taken from the same source.

study of the solubility of a gas in an aqueous solution. This has been done in the case of cane-sugar by Philip (1907). The solubility of hydrogen in cane-sugar solutions of various strengths was determined. From the decrease the degree of hydration of the cane-sugar was obtained.

To indicate the method of calculation, the solution containing 30·08 per cent. of cane-sugar may be taken. This absorbs 16·27 c.c. of hydrogen per 1,000 gms. of water. But pure water will absorb 18·83 c.c. of hydrogen per 1,000 gms. at the temperature used. Hence, the decrease is 2·56 c.c. The fraction of the total quantity of water attached to the sugar must be 2·56/18·83, and hence the number of water molecules attached to one molecule of cane-sugar is

$$\frac{2{\cdot}56 \times 69{\cdot}92 \times 342}{18{\cdot}83 \times 30{\cdot}08 \times 18} = 6{\cdot}00.$$

This evidence alone, of course, would be insufficient to enable us to assume that a definite hydrate of cane-sugar of the formula $C_{12}H_{22}O_{11}.6H_2O$ existed in solution, especially when it is noted that the molecular hydration decreases as the concentration of the solution increases.

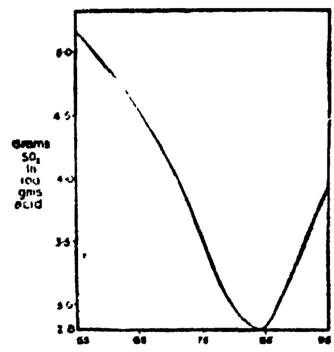


FIG. 127.—Solubility of Sulphur Dioxide in Sulphuric Acid.

The solubility of sulphur dioxide in solutions of sulphuric acid in water gives an indication of the existence of a hydrate of the formula $H_2SO_4.H_2O$, which is interesting because so many other properties of the aqueous solution of the acid show marked changes at this composition. Viscosity, density, optical properties, capillarity, specific heat and conductivity all show abrupt changes at a concentration 84·5 per cent. acid, 15·5 per cent. water, which corresponds to the monohydrate. If the solubility of sulphur dioxide in aqueous solutions of the acid is plotted against concentration of acid, a curve is obtained similar to that shown in Fig. 127.

Assuming that a solution of sulphuric acid in water consists of a mixture of the monohydrate and of water, the sulphur dioxide has the opportunity to dissolve in both of them. The solubility in an acid of the concentration required to give the pure monohydrate is 2·8 gms. of sulphur dioxide in 100 gms. of solution. From this, the solubility of the gas in acid of any strength can be calculated. Thus, the solubility of sulphur dioxide in sulphuric acid of strength 74·1 per cent. may be calculated. This will correspond to (100 ×

74·1)/84·5 = 87·68 per cent. $H_2SO_4.H_2O$. The free water present will then be 100 − 87·68 = 12·32 per cent. Now, the solubility of sulphur dioxide in pure water is known to be 10 gms. per 100 gms. of water. Hence, the 12·32 gms. of water will dissolve 1·232 gms. of the gas, and the sulphuric acid monohydrate will dissolve (87·68 × 2·8)/100 = 2·455 gms., making a total of 3·687 gms. The observed value was 3·63 gms. The following table gives the results for other concentrations, and the general agreement between the observed and calculated results gives support to the assumption made above, *viz.*, that aqueous solutions of sulphuric acid contain the monohydrate, and are, in fact, solutions of the monohydrate in water, and that the gas dissolves in both parts of the solution, the effect being additive.

TABLE LXX.—SOLUBILITY OF SULPHUR DIOXIDE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID. (Miles and Fenton.)

H_2SO_4 %	84·2	82·5	80·2	78·3	74·1	68·9	61·6	59·6
Sol. (calc.)	2·83	2·97	3·11	3·33	3·69	4·13	4·76	4·92
Sol. (obs.)	2·88	2·99	3·12	3·23	3·63	4·16	4·82	4·90

188. Effect of Temperature on Solubility.—When gases dissolve, there is usually an evolution of heat. On the basis of Le Chatelier's theorem (§ 138) it would therefore be expected that they would be less soluble at higher temperatures, and this is found to be the case. All gases except hydrogen and the inert gases, which have minima in their solubility curves, are less soluble as the temperature is increased. This is in marked distinction from solids, of which the reverse is usually, but not always, true. Solids usually dissolve with absorption of heat, and hence they are more soluble at higher temperatures.

When a solution of a gas is heated, the gas is usually expelled. If the gas obeys Henry's Law (§ 189), it should all be expelled at the boiling point of the liquid, if an open vessel is used. But it is extremely difficult to get rid of the last traces of a gas dissolved in water. Even after prolonged boiling water will contain traces of air.

Certain gases cannot be expelled when their solution is boiled, for they form constant boiling mixtures. An example of this is hydrogen chloride. If a dilute solution of this gas in water is boiled vapour richer in water will be given off first, until the solution remaining in the vessel has reached a certain strength (20·24 per

cent. at 760 mm.), when it will distil over as a whole, just as if it were a definite compound. The temperature at which this occurs is 110° C., when the pressure is 760 mm. If the acid solution which is heated is more concentrated than this to start with, vapour richer in acid will be given off first until there remains a liquid of the above composition, which will then distil unchanged. The fact that the composition of the constant boiling mixture varies with the external pressure applied indicates that it is not a definite compound, although for some time this view was held, especially as the composition of the mixture worked out almost exactly in agreement with the formula $HCl.10H_2O$.

The other halogen acids, and some other gases, form constant boiling mixtures which will be further discussed in connection with distillation (p. 434).

189. Henry's Law.—In the case of a solution of a gas in a liquid, we have present two phases—gas and solution. There are also two components—gas and solvent; so that, according to the Phase Rule,

$$P + F = C + 2,$$
$$2 + F = 2 + 2,$$

i.e.,
$$F = 2.$$

The system is therefore bivariant. Thus, if the temperature is fixed, both pressure of gas and composition of solution can vary. If the composition is fixed, pressure and temperature may be varied.

The connection between the pressure and composition of the solution is the most advantageous to study. This relationship was first noticed by Henry (1803), and was embodied in Henry's Law, which states that *the mass of gas dissolved by a given volume of liquid at constant temperature is proportional to the pressure of the gas.* Stated algebraically

$$\frac{m}{p} = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m is the mass of gas dissolved and p the pressure.

If we wish to deal with the volume of gas absorbed instead of the mass, this can easily be done by making use of the fact that the mass of a gas is proportional to its volume, by Avogadro's hypothesis, and is also proportional to the pressure, by Boyle's Law. Thus $m = pvK'$. Substituting in (1) we have

$$v = \frac{K_1}{K'} = K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

i.e., the volume of gas absorbed is independent of the pressure.

There is another form in which the law may be stated. Suppose the mass of gas absorbed in unit volume of the liquid is considered

Then the numerator of (1) will be the concentration of the gas in the solution, which may be called C_1. Now, the pressure of the gas is only another way of stating its concentration, so that instead of writing pressure p, we can write concentration C_2, and so we have

$$\frac{C_1}{C_2} = K_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

i.e., the concentrations of any single molecular species in two phases in equilibrium bear a constant ratio to each other at constant temperature. This is the generalised expression of Henry's Law.

A qualitative statement of Henry's Law can be derived from considerations of Le Chatelier's theorem (§ 138). According to this theorem, any system at equilibrium, when subjected to any constraint, will shift its equilibrium in such a way as to tend to annul the constraint. When we have a solution of a gas in equilibrium with the gas itself, if increased pressure is placed upon the gas, its volume would tend to get smaller; this would be aided by solution in the solvent, and hence the constraint would be annulled. Hence, the gas will be more soluble as the pressure is increased.

The law follows qualitatively also from considerations of the kinetic theory. If, again, a solution of a gas in some solvent is in equilibrium with the gas itself, and then additional pressure is applied to the gas, the result will be to increase the number of molecules hitting the surface of the solvent in unit time, and hence to increase the solubility.

Dalton showed that, in the case of a mixture of gases, Henry's Law applied separately to each gas, and that the pressure to be taken into account was the partial pressure of the gas in question, and not the total pressure.

This is illustrated in the case of air. Here we are dealing with a mixture of two gases (for simplicity), but the matter is complicated since the solubilities of the two gases are different. The partial pressures of oxygen and nitrogen in the air are in the ratio 1 : 4, but the solubility of oxygen is greater than that of nitrogen, so that the gas expelled from water on boiling, or on reducing the pressure, is relatively richer in oxygen than the original air was. If this gas is redissolved in water, and then boiled out again, it will be still richer in oxygen, and at one time it was proposed to make oxygen from the air in this way on the commercial scale. After eight absorptions, a gas containing almost 98 per cent. oxygen could be obtained.

That Henry's Law holds for other solvents besides water, providing physical solution only takes place, has been shown by numerous observers. Thus, the solution of hydrogen sulphide in aniline has been shown to obey the law closely (Bancroft and Belden,

J. Physical Chem., 1930, 34, 2123). This indicates that there is no compound formation in this case.

190. Experimental Verification of Henry's Law.—In the laboratory the law can easily be verified by the use of the ordinary apparatus for determining the solubility of a gas in a liquid. On altering the pressure, the volume of gas absorbed should remain constant.

The law has been verified by many investigators, one of the most recent determinations being that of Morgan and Richardson (1930) [1] who used oxygen. The following are some of the results :—

TABLE LXXI.—SOLUBILITY OF OXYGEN IN WATER AT DIFFERENT PRESSURES

Pressure, p. Cms.	Mass of gas dissolved in 1 litre of water, m. Gms.	m/p.
76·0	0·0408	0·0005369
61·0	0·0325	0·0005328
41·4	0·0220	0·0005314
30·0	0·0160	0·0005333
17·5	0·0095	0·0005429

The above determinations were made at 25° C. If Henry's Law is true, the values given in the last column of the table should be constant. This is so, within the limits of experimental error. It has been shown by many others that the law holds when there is physical solution ; but, when there is compound formation, association or dissociation, the law must be modified. It should be pointed out, however, that deviations from the law are encountered even with physical solution. It has recently been shown that the nature of the deviations depends not only upon the gas, but also upon the solvent. The solubility of argon, for example, in water, methyl and ethyl alcohols, pentane and other organic liquids, shows deviations from Henry's Law which are negative for water and positive for the alcohols. Such deviations cannot be accounted for by the imperfect nature of the gases. Like Boyle's Law, Henry's Law can only be true for ideal gases, and ideal solutions (*i.e.*, those in which there is no compound formation), but in the examples now considered deviations due to the non-ideal nature of the solution are insufficient in magnitude to account for the differences observed.

[1] For an account of the accurate determination of gaseous solubility, see the papers by Morgan and co-workers on the solubility of oxygen in various solvents in *J. Physical Chem.*, 1930, 34, 1578, 1818, 2045, ...

191. Deviations from Henry's Law.[1]—There are three ways in which solution can take place, in addition to ordinary physical solution. There may be compound formation between the solvent and the gas; there may be association of the gas into more complex molecules; or there may be electrolytic or other dissociation of the substance (§ 251). Sometimes more than one of these possibilities is met with for the same solution.

Now the guiding principle to be borne in mind throughout this work is that Henry's Law only holds when the *same molecular species* is considered in the two phases. Even though solution does take place in an abnormal fashion according to one or more of the above methods, we can still apply Henry's Law if we consider the molecular species present that are identical.

(1) *Compound Formation.*—The equilibria are represented by

$$\underset{\text{Gas phase.}}{X} \rightleftharpoons \underset{\text{Liquid phase.}}{X + nS \rightleftharpoons X\,.\,nS.}$$

Actually in the solution there will be an equilibrium between the compound and the solvent and gas. This will be governed by the Law of Mass Action (§ 153).

Let C_1 = concentration of gas molecules in the gaseous phase,
C_2 = concentration of gas molecules in the liquid phase,
C_3 = concentration of solvent molecules,
C_4 = concentration of compound molecules.

By Henry's Law

$$\frac{C_1}{C_2} = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By the Law of Mass Action

$$\frac{C_2 \times C_3{}^n}{C_4} = K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now C_3 will be very large, and can be written as a constant. Hence,

$$\frac{C_2}{C_4} = K_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Inverting this equation, we have,

$$\frac{C_4}{C_2} = \frac{1}{K_3}$$

$$\therefore \quad \frac{1 + K_3}{K_3} = \frac{C_4 + C_2}{C_2}$$

$$\therefore \text{ from (1) } \frac{C_1}{C_4 + C_2} = \frac{K_1 K_3}{1 + K_3} = K_4 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

[1] This paragraph requires a knowledge of several points dealt with later in the book, and is best postponed until a second reading.

i.e., the ratio of concentration of molecules in the gas phase to the total concentration of gas molecules, both free and compound, in the liquid phase is constant. This latter is the concentration of gas in the liquid phase as determined by analysis, and so, if Henry's Law is applied to this system in the usual way, it will give an answer which is apparently correct. It is to be noted, however, that the constant obtained will have a different value from that which would be obtained if the law were applied to the true gas molecules which are dissolved, but this is the only difference. An example of a gas which follows this equation is carbon dioxide. The amount of electrolytic dissociation occurring here is so small as to be negligible.

TABLE LXXII.—APPLICATION OF HENRY'S LAW TO THE SYSTEM CARBON DIOXIDE-WATER

Temp., °C.	Pressure of Gas, p. Metres of Hg.	Wt. of Gas dissolved, m. Gms.	$K_1 = m/p$.
19·9	0·7255	38·61	52·49
	0·5245	27·24	51·94
	0·5237	27·08	51·71
	0·5231	27·28	52·13
3·2	0·5244	31·41	58·53
	0·6467	38·66	59·78
	0·6470	38·49	59·48

If, however, the compound formation is accompanied by dissociation, the case is quite different.

(2) *Dissociation*.—The equilibria now present are

$$\underset{\text{Gas phase.}}{XY} \rightleftharpoons \underset{\text{Liquid phase.}}{XY \rightleftharpoons X^+ + Y^-}.$$

Let α be the degree of dissociation, and the above symbols still retain the same significance, and let C be the total concentration in the liquid phase.

Henry's Law states,

$$\frac{C_1}{C_2} = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The Law of Mass Action states

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence,

$$\alpha = \frac{-K_2 \pm \sqrt{K_2^2 + 4K_2C}}{2C} \quad . \quad . \quad . \quad . \quad (3)$$

The negative value of the quantity under the square root sign is inadmissible.

$$K_1 \quad \frac{C_1}{C_2} = \frac{C_1}{C(1-\alpha)} = \frac{2C_1}{2C + K_2 - [illegible]} \quad . \quad (4)$$

If this is to be tested experimentally, it is necessary to know the equilibrium constant K_2. C_1 and C are obtained by analysis. This theory has been tested experimentally in the case of ammonia gas dissolved in water. Here the equilibria are

$$NH_3 \rightleftharpoons NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-,$$

but the formation of the compound, NH_4OH, has no effect on the form of the equations, making a difference only in the numerical value of the constant. There is satisfactory agreement. Some of the results are shown in the accompanying table, due to Calingaert and Huggins (1923).

TABLE LXXIII.—THE SYSTEM AMMONIA-WATER AT 100° C.

C.	$K = \frac{C_1}{C}$.	$1-\alpha$.	$K_1 = \frac{C_1}{C(1-\alpha)}$.
1·256	12·92	0·987	13·1
0·633	12·67	0·981	12·9
0·148	12·13	0·963	12·6
0·0386	12·06	0·926	13·0
0·0107	11·53	0·864	13·3

The case of association can be treated in an exactly similar manner. The whole question of deviations from Henry's Law has received much attention, and it is clear that, like the other gas laws, it can only be applied to what have been called ideal gases.

Where the degree of dissociation is large, the calculation can be simplified. If the concentration of single molecules in the gaseous phase is C_1, and that in the liquid phase is C_2, $C_1/C_2 = K$. Now suppose that dissociation takes place into two individuals. If C_3 is the concentration of each new species, by the Law of Mass Action, $C_2 = K_1C_3^2$. Hence, the concentration of the single molecules, assuming dissociation to be large, will be proportional to the square of the concentration of the new species, which in this case is the quantity measured. Hence,

$$\frac{C_1}{K_1C_3^2} = K$$

$$\frac{C_1}{C_3^2} \quad KK_1$$

In the case of association, let the concentration in the gas phase be C_1, whilst the concentration in the second phase is C_2; and let n be the number of simple molecules in the associated complex. If the concentrations of single and associated molecules in the liquid phase are s and a respectively, then by the Law of Mass Action $s^n = Ka$, or $\frac{s}{\sqrt[n]{a}} = C$. The concentration of single molecules in the liquid phase is thus proportional to the nth root of the concentration of the complex molecules, which is actually measured, and Henry's Law takes the form,

$$\frac{C_1}{\sqrt[n]{a}} \quad K.$$

C. SOLUTIONS OF GASES IN SOLIDS

192. Types of Solution.—Gases are frequently taken up by solids, *e.g.*, palladium takes up hydrogen, and charcoal absorbs many gases.

There are four ways in which this may occur. Strictly speaking, it is not correct to term all these different ways solutions, but it will be better for our purpose if they are all considered here.

In the first place, a gas may dissolve in a solid to give a perfectly homogeneous solution in which there has been no alteration in the constitution or composition of the gas at all. This is a case of true solution, and the laws which govern this phenomenon are similar to those which govern the solution of gases in liquids.

Secondly, two or more solid solutions may be formed, and these may be only partially miscible, or completely immiscible, with each other.

Thirdly, a chemical compound may be formed between the gas and the solid.

Finally, the gas may be adsorbed by the solid. By the term "adsorption" we mean taking up on the surface only. When a gas is adsorbed by a solid it forms only a surface layer. It is true that this is usually accompanied by a slow diffusion of the gas to the interior of the metal, but at first the gas is concentrated at the surface. Adsorption is an extremely important phenomenon and comes into play not only here, but also in the solution of solids in liquids, and in other cases. It largely explains the catalytic activity of powdered and finely divided metals, as will be explained in a later section (§352).

To decide in which of these four ways a gas has been taken up by a solid, the Phase Rule will be found especially useful.

193. True Solution.—In the case of a gas dissolving in a solid to form a true solution, Henry's Law will apply. As in the consideration of the solution of gases in liquids, the number of phases is two, and the components two. Hence, the number of degrees of freedom is also two. If the temperature is kept constant, both composition of the solution and the pressure can be altered, but one will depend upon the other. The concentration (C) and pressure (P) will be related by the equation

$$\frac{P}{C} = K.$$

If then the pressure is plotted against the composition of the solution, a straight line will be obtained, as shown in Fig. 128.

If, however, the gas changes its molecular condition when it dissolves in the solid, the relationship is, as in the case of the system, gas-liquid,

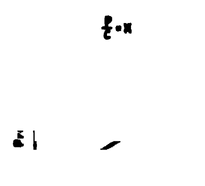


Fig. 128.

$$\frac{P}{\sqrt[n]{C}} = K$$

when association into molecules of n times the molecular weight takes place in the solid, and

$$\frac{P}{C^n} = K$$

when dissociation of the molecule into n parts takes place in the solid (§ 191).

194. Formation of Solid Solutions.—It is possible for a gas to dissolve in a solid to form a solid solution, and when the concentration reaches a certain value a new solid solution may be formed which is not miscible with the first. As soon as this happens we have two solid phases, and one gas phase, making a total of three, whilst the number of components remains two. Hence, the number of degrees of freedom is one, *i.e.*, only *one* variable can be fixed arbitrarily. If the temperature is fixed, then the pressure and compositions of the phases are automatically fixed too.

If a graph is drawn between pressure of the gas and concentration (the amount of gaseous component in the system) at constant temperature, it is found to be of the form shown in Fig. 129. The portion ab represents the formation of the first solid solution. This is a straight line, governed by the equation $P/C = K$. There are two degrees of freedom, since we have two phases (solid and gas). One degree is lost in fixing the temperature, and so there is one left, *i.e.*, to each concentration there is a definite pressure, giving the curve ab. At b the new solid solution makes its appearance, and

there are now three phases, and only one degree of freedom in the system. As the temperature is fixed, there are no degrees of freedom left at all, and so the next part of the curve is a straight line parallel to the concentration axis. Addition of one or other component now merely alters the relative amounts of the phases, leaving their compositions and the gas pressure constant. It may be that as the concentration of gas is increased the first solid solution disappears, as it is completely converted into the second, and then there are only two phases again, and the curve would be of the form *cd*.

195. Formation of Chemical Compounds.—If a gas forms a compound with a solid, admission of large quantities of gas will fail to produce any great pressure of gas over the solid, since the dissociation pressures (§ 160) of solids are usually low at ordinary temperatures. When, however, all the solid has been converted into the compound, it may be incapable of absorbing more, or the new compound may act like the original solid and give solid solutions with the gas, or form another higher compound. If that is so, the phenomenon is governed by exactly the same considerations as those already stated, the compound being regarded for this purpose as a pure solid.

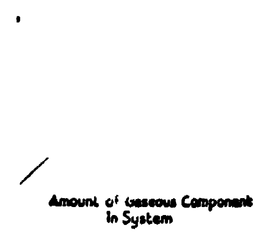


FIG. 129.

196. Adsorption.—This is the most important case of all, and the one usually met with when a gas is "taken up" by a solid. It is well known that glass and porcelain have the power of taking up moisture from the atmosphere. It is extraordinarily difficult to remove this film of moisture. To remove it completely it is necessary to heat the vessel to redness *in vacuo*. It is a surface effect, and hence finely divided solids will be more active in taking up gases in this way than an ordinary solid. Thus, platinum black, finely divided nickel, copper powder, animal charcoal and other kinds of charcoal are especially active as adsorbing agents.

When a gas is brought into contact with some such agent, a condition of equilibrium is set up almost immediately. A certain amount of gas is adsorbed at a given pressure, and if the pressure is altered either more gas is taken up or some is expelled. The fact that equilibrium is instantaneous points to the phenomenon as being a surface effect, for molecules can diffuse only slowly through a solid. After a time, however, a further small amount of gas can be taken up, showing that there is a slow diffusion of the gas into the interior of the adsorbent.

A study of the amount of gas adsorbed by a given surface under different pressures shows that the relationship

$$\frac{x}{m} = ap^b$$

holds. In this equation, x is the weight of gas adsorbed by m gms. of solid at pressure p, a is a constant dependent upon the surface, and b a constant dependent upon the gas. b is always less than unity.

A comparison of this expression, which is called the *adsorption isotherm*, with Henry's Law shows that the two are alike in form. Henry's Law may be written in the form

$$\frac{x}{m} = ap,$$

x being the amount of gas dissolved by m gms. of liquid at a pressure p, and a being a constant. We have seen that when the pressure is raised to a power it indicates a change of molecular state of the gas in the solvent. The formula employed when dissociation takes place in the solvent is

$$\frac{C_1}{C_2^n} = K, \text{or } \frac{x}{m} = ap^n,$$

and when association takes place

$$\frac{C_1}{\sqrt[n]{C_2}} = K, \text{or } \frac{x}{m} = ap^{\frac{1}{n}}.$$

Hence, it might be concluded that we are dealing in this matter of adsorption with a change of molecular state of the gas when it is taken up by the solid, and, since the power b is always less than unity, the molecular weight in the adsorbed state must be less than in the gaseous state. Actually b comes out at 0·44 for ammonia, 0·39 for carbon dioxide, and 0·12 for chloroform. These values would give impossible figures for the molecular weight in the adsorbed state, so we are forced to conclude that the adsorption isotherm is an expression of an entirely different nature from Henry's Law. It is, in fact, merely empirical (§ 346).

197. The Mechanism of Adsorption.—Adsorption is due to surface forces. In dealing with surface tension it was pointed out that the surface forces were due to unbalanced molecular forces. In the bulk of a liquid a molecule is surrounded on all sides by other molecules, and consequently it attracts, and is attracted, in all directions equally ; but in the surface layer the molecules are only subjected to fields of force over a part of their surface, and so there is the development of surface energy.

A very similar explanation can be given for adsorption. The

atoms in a solid are held in position in the space lattices (§ 124) by attractive forces between neighbouring atoms. At the surface, however, they are only held on one side, and so there will be a certain amount of surface energy latent. A gas molecule will be held by the atom with this extra force, and will thus be adsorbed. If the gas molecule itself possesses a certain amount of affinity for the solid, it will be held relatively firmly, and, indeed, chemical reaction may take place ; but if its affinity for the metal is small or negligible, the only force holding the gas atom on to the metal is the unsatisfied crystal force mentioned above, and slight thermal agitation will be sufficient to remove it.

Langmuir, in accordance with this theory, believes that there are certain points on a solid surface where this additional force is centred. These points have a definite relationship to the crystal lattice. When a gas is admitted to a vessel containing the solid,

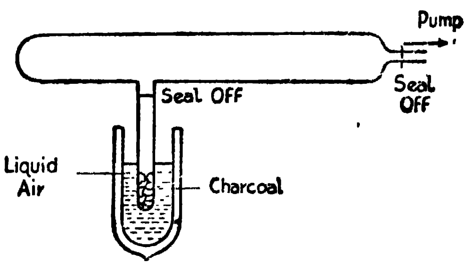


FIG. 130.

which has been previously outgassed by heating to redness in a vacuum, it is adsorbed at these points. The pressure may not be sufficient to cause all the vacant spaces to be occupied, so that on increasing the pressure a further amount of gas is adsorbed. Ultimately, however, all the available spaces are filled, and the surface is covered with a layer of gas one molecule thick. It has been shown experimentally that in many cases of adsorption of gases the adsorbed layer is unimolecular.

When dealing with some of the gases which are most easily liquefied, or with others which are near their critical point, the adsorbed layer may be more than one molecule thick, for at this stage there are attractive forces between the molecules of the gas themselves, which will enable thicker layers to be built up. It is for this reason that the more easily liquefied gases, such as ammonia and carbon dioxide, are the more readily adsorbed by agents such as charcoal.

The fact that a gas is more easily adsorbed when it is nearing

liquefaction is made use of in the high evacuation of tubes for spectroscopic work. First as much air as possible is removed from the tube (which is provided with a side-tube containing coconut charcoal, a specially active adsorbent) by means of an air-pump. Then the tube containing the charcoal is placed in a Dewar vessel containing liquid air (Fig. 130). The charcoal adsorbs almost entirely the gas which is left, enabling a much higher vacuum to be obtained than would be possible by means of a pump alone.

The fact that finely divided metals are good catalysts in various reactions can be explained as an adsorption phenomenon, and for this reason the study of adsorption is of great importance. It will be further discussed in Chapters XVII and XVIII.

198. The Occlusion of Hydrogen by Palladium.—One of the most interesting cases of the solution of a gas in a metal is the occlusion of hydrogen by palladium. This phenomenon was first observed in 1866 by Graham, who found that palladium foil which had been previously heated to redness in a vacuum would take up 376 times its volume of hydrogen at room temperatures, 643 times at 90°–97° C. and 526 times its volume at 245° C.

The amount of gas taken up, however, depended upon the pressure, and upon the physical state of the metal. Graham believed that the hydrogen was condensed to a sort of metal, to which he gave the name "hydrogenium," and that this formed an alloy with the palladium.

Troost and Hautefeuille in 1874 studied the effect of pressure on the occlusion. At a given temperature (say 120° C.) they found that at first the pressure increased as the concentration of gas in the metal increased, but that on further addition of hydrogen the pressure remained constant. On still further increasing the concentration of hydrogen, the pressure rose. The same thing happened at other temperatures. The results are embodied in the curves drawn in Fig. 131.

The first part of the curve, *ab*, would correspond to physical solution of the hydrogen in the metal (cf. Fig. 128). Troost and Hautefeuille considered that the straight portion, *bc*, which followed indicated the formation of a chemical compound, which, when all the palladium had been converted into it, could itself take up hydrogen, thus accounting for the renewed rise in the curve, *cd*. The palladium had taken up 600 volumes of hydrogen at the commencement of the second rise. The density of palladium is 12, so that the ratio of the weights of metal and gas in the substance formed is $12 : 600 \times 0{\cdot}00009 = 12 : 0{\cdot}054$. The atomic weight of palladium is 106. If the substance is a definite chemical compound its formula will be obtained by dividing these ratios by the atomic

weights. The values 2·03 : 1 are obtained, which would make the compound Pd_2H. As will be seen, it is a mere coincidence that this is a simple ratio.

However, simply because the pressure remains constant whilst the composition varies, it cannot be argued that a compound is present. It is equally possible, as Hoitsema showed, to have two non-miscible solid solutions. We have already seen that this would give a curve of the nature required (§ 194).

It is necessary to find some way of distinguishing the two cases, so that it may be known definitely whether it is a matter of formation of a compound, or two non-miscible solid solutions. This can be done from a study of the pressure-composition curves for different temperatures. If a chemical compound is present, the pressure remains constant whilst the metal takes up more and more hydrogen until all the metal is converted into compound, after which it again rises. The concentration at which the second rise begins should be the same at all temperatures unless different compounds are formed at different temperatures. There are only certain possibilities of this, and it must be assumed that one compound would be stable above a certain temperature, and another below it, in which case the concentration at which the second rise begins should be constant up to a certain temperature, and then suddenly take up another definite value.

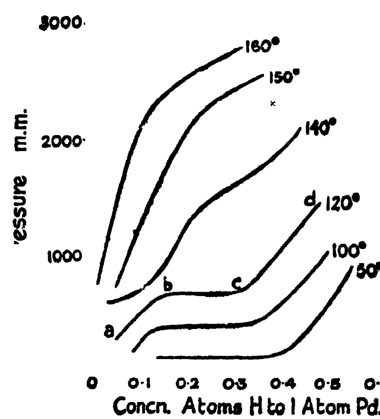


FIG. 131.—Relationship between Pressure and Concentration in the Palladium-hydrogen System.

If two non-miscible solid solutions are being dealt with, the concentration at which the second rise begins, *i.e.*, the concentration at which the solutions become completely miscible, and therefore exist as one phase, will vary continuously with temperature. A glance at the curves in Fig. 131 will show that this second case is correct, and that we are dealing with two non-miscible solid solutions.

A good deal of work has been done to discover more about these solid solutions, and the conclusion has been drawn that they are in effect a solution on the surface, and a solution in the interior of the metal. The latter does not appear to be homogeneously distributed through the metal. The surface layer can be removed fairly easily

by pumping, but it is much more difficult to remove the hydrogen in the interior. *X*-ray analysis (§ 125) of the palladium which has adsorbed hydrogen fails to show any change of structure at the beginning of the portion of the curve *bc*. A change would be expected if compound formation occurred.

D. SOLUTIONS OF LIQUIDS IN LIQUIDS

199. General.—It was a tenet of the alchemists that *similia similibus solvuntur* (like is dissolved by like), and this appears to be generally true. Thus, water will dissolve alcohol to any extent, but will not mix with mercury. Mercury, on the other hand, will dissolve metals. Benzene will not dissolve water, but will dissolve hydrocarbons.

This generalisation has received some theoretical explanation from the electronic theory. It is found that liquids tend to fall into two classes, water and the hydrocarbons being the extreme members of each class. Liquids of the water class dissolve in each other, but as a rule will not mix with those of the hydrocarbon class. The liquids of the water class are all ionising solvents, they have higher dielectric constants than the other liquids (a property which makes them ionising solvents), they tend to polymerise in solution, and in the pure liquid state, and they have abnormally high boiling points. The liquids of the water class are termed " abnormal," whilst those of the hydrocarbon class are " normal." Sometimes the terms " polar " and " non-polar " respectively are met with to indicate the same liquid classes ; but these terms are strictly speaking incorrect, and should be avoided. Generally, associated substances are co-ordinated compounds (§ 61).

All non-associated liquids are completely miscible with each other, and all the extreme members of the associated class, *e.g.*, water and the lower alcohols, are completely miscible. If, however, we bring together a liquid of one class and one of the other, they will usually not dissolve. Since there is this difference between molecules of the different classes, it is clear that the deciding factor is the nature of the electric fields of the molecules. In associated molecules there must be electrical forces which tend to keep the molecules together, and these give rise to an internal pressure. In normal molecules there is a very weak external field, so that if a normal substance is mixed with an associated one there will be a tendency for the two types to separate, and solution does not occur. The associated molecules will tend to remain as such and not be broken into by the normal molecules.

200. The System Phenol-Water.—If phenol is mixed with water,

two liquids are produced, one a solution of phenol in water, and the other a solution of water in phenol. These two form separate layers. Now, at any given temperature the composition of these layers is fixed. On warming, the amount of water in the phenol phase increases, and the amount of phenol in the water phase increases, until at a certain temperature the composition of both layers becomes the same. Then, of course, there will be complete miscibility ; there will be no separation of the liquid into two layers. The system was studied by Rothmund in 1898, and the following data are due to him. They are plotted in the curve shown in Fig. 132.

TABLE LXXIV.—THE SYSTEM PHENOL-WATER (Rothmund)

Temperature, °C.	10	20	30	40		55	60	65	68·4
Wt. per cent. phenol in aqueous phase	7·5	8·5	8·7	9·7	12·0	14·2	17·5	22·7	36·1
Wt. per cent. phenol in phenol phase	—	72·2	69·9	66·8	62·7	60·0	56·2	49·7	36·1

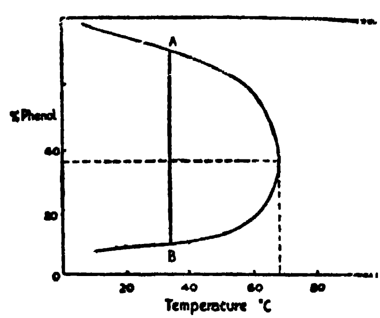


FIG. 132.—Solubility of Phenol in Water and of Water in Phenol.

The temperature at which the two phases disappear and one takes their place is called the *critical solution temperature*, and sometimes the *consolute temperature*. Since it is possible in some systems (§ 202) to have a lower temperature of a similar nature, it is also frequently called the upper critical solution temperature.

The solubility curve drawn in Fig. 132 is parabolic in shape (approximately), but no general formula has been derived by means of which this curve can be represented to cover all cases. Its shape,

and the nature of the phenomenon with which it has to deal, recall the method of Cailletet and Mathias for determining critical volume (§ 85). At any definite temperature, the compositions of the two layers will be represented on opposite branches of the parabola. The line joining them, *e.g.*, AB in Fig. 132, is called a *tie-line*, and the two solutions are said to be *conjugate*.

The critical solution temperature is affected very much by the presence of impurities, and may be used as a criterion of purity. For phenol, the effect of the addition of small quantities of benzene, naphthalene and pyridine is to raise the critical solution temperature. The criticism has recently been made that Rothmund's value of the critical solution temperature of phenol is too high owing to the phenol used being not quite pure. According to Dolique (*Comptes rendus*, 1932, **194**, 289), the critical solution temperature of the purest phenol is $66{\cdot}5 \pm 0{\cdot}1°$ C., and the concentration at this temperature is 34·0 per cent.

201. The System Triethylamine-Water.—Here the reverse behaviour is encountered. Below 18·5° C. the two liquids are completely miscible, but above it they form two distinct layers. This system was studied by Rothmund, whose figures are given below, and are plotted in Fig. 133. Nearly all the substances which show this

TABLE LXXV.—THE SYSTEM TRIETHYLAMINE-WATER

Temperature, °C.	70	50	30	25	20	18·5
Wt. per cent. amine in aqueous phase	1·6	2·9	5·6	7·3	15·5	c. 30
Wt. per cent. amine in amine phase	—	—	96	95·5	73	c. 30

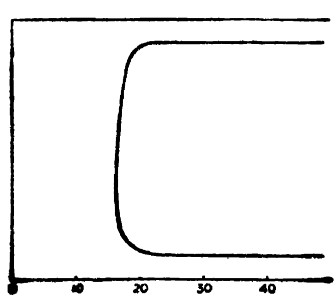


FIG. 133.—Solubility of Triethylamine in Water, and of Water in Triethylamine.

behaviour with water are amines, and they are not easy to obtain in a state of purity. As impurities have a considerable effect on the critical solution temperature (§ 200), it is a difficult matter to obtain accurate results in this work.

202. The System Nicotine-Water.—In this case we have a closed solubility curve. There are two critical solution temperatures—an upper and a lower. The figures obtained by Hudson (1903), and confirmed by Tsakalotos (1909) are given below, together with the graph.

TABLE LXXVI.—THE SYSTEM NICOTINE-WATER

Per cent. nicotine by wt.	6·8	7·8	10·0	14·8	32·2	49·0	68·8	80·2	82·0
Lower Temperature, °C.	94	89	76	65	61	64	72	87	129
Upper Temperature, °C.	95	155	—	200	210	205	190	170	130

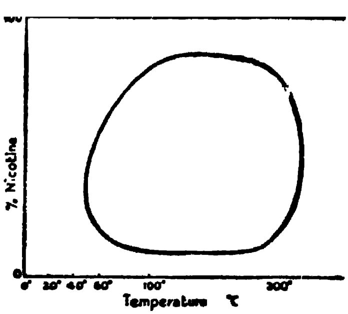


FIG. 134.—Solubility of Nicotine in Water and of Water in Nicotine.

It was found by Tsakalotos that the composition for the two critical points (60·8° C. and 208° C.) is the same. Between these temperatures two layers are obtained, but outside them there is complete miscibility.

It is interesting to note the effect of pressure on this system. Application of pressure raises the lower, and decreases the higher critical solution temperature, so that the area of the closed ring gets smaller and smaller, until finally it becomes a point, and the liquids are completely miscible over the whole range of temperature.

203. Experimental Methods of studying Mutual Solubility.—The simplest method is that used by Alexejew. Known amounts of the two liquids are introduced into tubes which are then sealed and

placed in a water-bath, of which the temperature is gradually increased. The temperature at which the two layers disappear in the tubes is noted. The tubes must be shaken frequently during the experiment. In this way a series of points on the mutual solubility curve is obtained.

Another method is to take amounts of the liquids and shake them together in a tube placed in a thermostat. When equilibrium has been attained, known volumes of each layer are analysed. This method is not easily carried out, as in some cases the analysis is difficult.

A thermostatic method devised by Hill (1923) is of interest. The two components are weighed into each of two vessels in differing amount, and the volumes produced after equilibrium has been reached at a fixed temperature are measured. Graduated cylinders may be used for this purpose. Let m_1 and m_2 be the weights of the first component used in the two experiments, and c its concentration in grams per c.c. at equilibrium in the upper phase, and d its concentration in the lower phase. If the volumes of the upper phase are v and v_1 and of the lower w and w_1,

$$cv + dw = m.$$
$$cv_1 + dw_1 = m_1.$$

If these equations are solved for c and d, the concentration of the first component in each phase is determined. Similar equations are used for the second component. Adding the amount of each component present in a given phase, we have the weight per c.c., or the density, and the percentage composition by weight is obtained.

204. The Vapour Pressures of Solutions of Liquids in Liquids.—It is necessary to deal separately with the three types of solution: (*a*) components completely miscible, *e.g.*, alcohol and water; (*b*) components partially miscible, *e.g.*, ether and water; (*c*) components practically immiscible, *e.g.*, nitrobenzene and water. The liquids are not absolutely immiscible, but there are always two liquid phases over ordinary concentration ranges.

205. Components Completely Miscible.—Applying the Phase Rule to this case, we have two components and two phases, so that the system is bivariant. This means that if the temperature is fixed the other remaining degrees of freedom, *i.e.*, pressure and composition, must vary together. Thus a mixture of any given composition will have a fixed and definite vapour pressure at a given temperature.

If the vapour pressure of a liquid mixture is plotted against the composition, the curve obtained will be one of five types which are shown in Fig. 135.

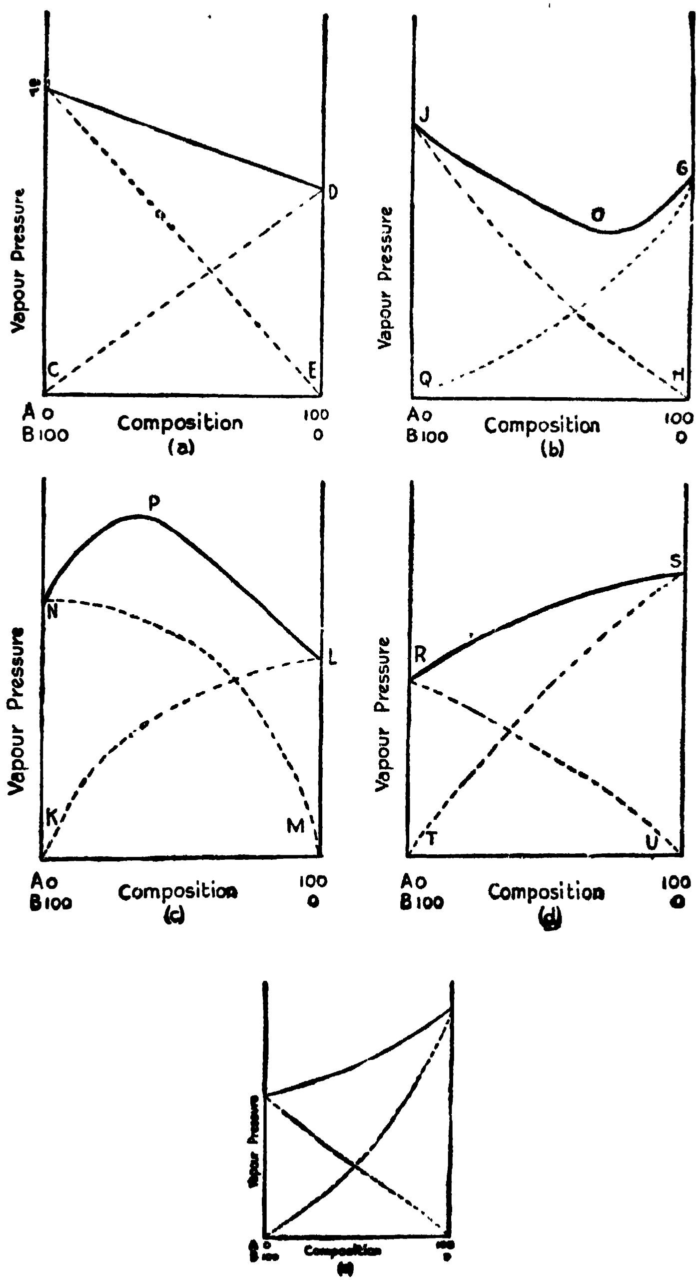


Fig. 135.—Types of Vapour Pressure-composition Curves for Completely Miscible Liquids.

(*a*) In the first case the vapour pressure curve is a straight line. The two dotted lines represent the partial pressures of the components. These are both straight lines and indicate that both components are ideal liquids, obeying Raoult's Vapour Pressure Law (p. 477), which states that the relative lowering of the vapour pressure of a solution is equal to the ratio of the number of molecules of solute and of solvent in the solution. Such liquids are those drawn from the normal class, and which do not form compounds with each other, or cause polymerisation or dissociation.

Examples would be mixtures of benzene and toluene, and benzene and hexane. The total vapour pressure of the liquid will be the sum of the partial pressures of the separate vapours and is given by the line FD. Consider the vapour from a mixture of this kind. It will contain each constituent in the proportion of its partial pressure, and will therefore contain more of the more volatile component. Suppose that, by condensation in a separate vessel, this vapour is removed, then the condensed liquid will contain more of the more volatile component, and the liquid left behind in the flask will contain more of the less volatile component. By repeated vaporisation and condensation, *i.e.*, distillation, it would be possible to effect a separation of the two components, and this is what happens in fractional distillation. This process, however, will be fully dealt with in a later section (209).

If the lines CD and EF were slightly curved, they would give when added a total vapour pressure curve which did not possess any definite maximum or minimum, as in (*d*) and (*e*), and the same considerations would apply.

(*b*) In the second case the total vapour pressure curve exhibits a minimum, and this can be made up of two partial pressure curves which are concave upwards, or one straight line and one concave curve. Suppose we take a liquid mixture belonging to this class which has an excess of B, the more volatile component. When this is distilled the vapour will contain an excess of B, and so the residue in the flask will gradually get richer in A. Ultimately, the mixture with the lowest vapour pressure, and hence the highest boiling point, will be reached, and this will distil over unchanged. If the mixture is rich in A the same thing takes place; A distils over first, and then the constant boiling mixture. It is therefore impossible to separate this mixture into its components by fractional distillation. The best that can be done is to separate it into one component, and the constant boiling mixture. Examples of this behaviour are furnished by the common acids. Sulphuric acid and water form a constant boiling mixture, boiling at 338° C., and containing 98·7 per cent. of the

acid. Hydrochloric acid forms a constant boiling mixture distilling at 110° C. and containing 20·24 per cent. of the acid (p. 414).

(*c*) Here the mixture gives a maximum in the total vapour pressure curve. The mixture which has the maximum vapour pressure will obviously boil at a lower temperature than any other mixture, and so, on distilling a mixture of this type, the maximum vapour pressure mixture will come over first, until all of one component has been used up. Then the temperature will rise and the other component will distil. It is again impossible to effect a separation by fractional distillation. All that can be done in this direction is to separate it into a constant boiling mixture and one component. A good example of this is the mixture of ethyl alcohol and water. This forms a mixture of minimum boiling point, 78·13° C., which contains 95·59 per cent. alcohol. This accounts for the great difficulty encountered in preparing absolute alcohol. By ordinary distillation of a mixture of alcohol and water, alcohol of strength 95·59 per cent. comes over. To obtain pure alcohol from this, the water must be removed by chemical means, *e.g.*, by the addition of calcium oxide, anhydrous copper sulphate, and, finally, metallic calcium. With the water thus chemically bound, it is possible to distil off pure alcohol. Mention may here be made of another method of dehydrating alcohol, used on the commercial scale. If benzene is added to a mixture of alcohol and water, the benzene forms a low-boiling mixture with the water, and some of the alcohol, and on distillation this comes over first. In this way, the water is removed from the alcohol, and the mixture left in the distilling vessel contains benzene and alcohol, which can be separated by distillation.

0 H_2O
100 Et_2O

FIG. 136. — Vapour Pressure-composition Curve for a Mixture of Partially Miscible Components.

Pyridine and water afford another example of a minimum boiling mixture.

206. Vapour Pressure Curves of Partially Miscible Liquids.—A mixture of ether and water may be taken as an example. The curve is shown in Fig. 136.

When ether is added to water it first of all dissolves. If a small quantity of ether is added to water a true solution is formed, and the total vapour pressure of the mixture increases as shown by the line AB. But, as more ether is added, the water becomes saturated, and a layer of ether is formed, *i.e.*, a new phase is produced. Now,

according to the Phase Rule, the system must become univariant, for we have three phases (ether in water, water in ether, vapour) and two components (ether and water). This means that the vapour pressure will remain constant whilst the composition varies. This is the line BC in the curve. At a point C, sufficient ether will have been added to dissolve all the water, and there is now a saturated solution of water in ether. From this point the vapour pressure will rise to that of pure ether at D. In other cases the curve falls as in the lower curve A^1 B^1 C^1 D^1.

207. Vapour Pressure of a Mixture of Immiscible Liquids.—It is obvious that here we have three phases throughout the whole range of compositions, and two components. Hence, according to the Phase Rule, the system is univariant, and vapour pressure is constant for all compositions. It is therefore a straight line curve parallel to the composition axis. The curve is really the same as that just considered (Fig. 137), except the sloping portions have become very short.

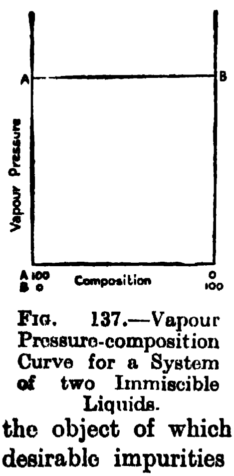


FIG. 137.—Vapour Pressure-composition Curve for a System of two Immiscible Liquids.

The vapour pressure AB will be the sum of the partial pressures of the two components. Thus, at a temperature of 80° C., the vapour pressure of water is 356 mm., whilst that of bromobenzene is 66 mm. The vapour pressure of a mixture of these two would therefore be 422 mm. at 80° C.

208. Steam Distillation.—This property of a mixture of immiscible liquids is made use of in the process of steam distillation, the object of which is to separate organic substances from undesirable impurities which would be difficult to remove in other ways, or to distil an organic body without submitting it to too great a temperature or resorting to vacuum distillation.

The apparatus is illustrated in Fig. 138. It consists of a boiler A, the steam generated therein being passed into the large flask B containing the mixture to be separated. This is connected by an outlet tube to a Liebig's condenser in the usual way. Finally, to obtain the product pure it must be separated in a separating funnel from the water which also comes over, and then dried and redistilled.

The amounts of water and substance which distil over can readily be calculated. Suppose that, at the boiling point of the liquid, the vapour pressures of the two components are p_1 and p_2. The volumes of vapour produced will be proportional to these pressures. The densities of the vapours are proportional to their molecular

weights, so the ratio of *weights* of the substances distilling is $\frac{M_1p_1}{M_2p_2}$, M_1 and M_2 being the molecular weights of the liquids.

This is best illustrated by a numerical example. A mixture of nitrobenzene and water boils at 99° C. The molecular weight of nitrobenzene is 123, and the vapour pressure of water at 99° C. is 733 mm. Hence, the vapour pressure of the nitrobenzene must be 27 mm. The ratio by weight in which the two liquids distil is

$$\frac{\text{Nitrobenzene}}{\text{Water}} = \frac{123 \times 27}{18 \times 733} = \frac{1}{3 \cdot 97}.$$

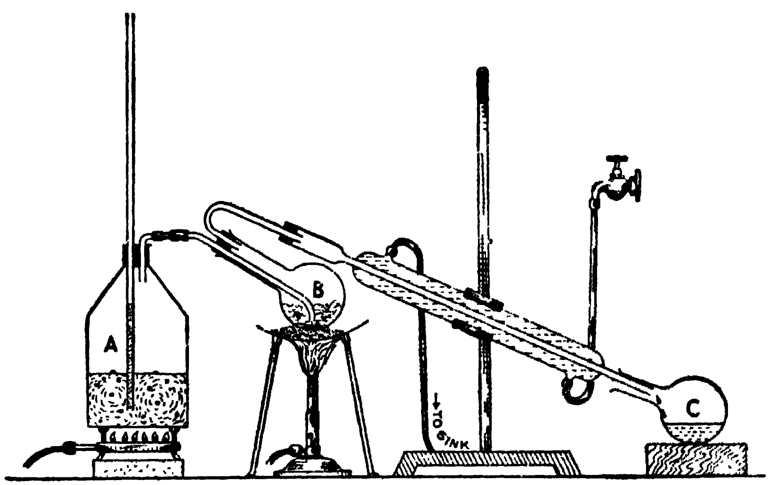


FIG. 138.—Apparatus for Steam Distillation.

It is obvious that water is a good liquid to use in this connection, because it has a low molecular weight.

The reverse calculation is sometimes used for finding the molecular weight of a liquid which is not miscible with water. Thus, a mixture of bromobenzene and water distils at 95·2° C., at which the respective vapour pressures are 119 and 641 mm. The ratio by weight in which the liquids distil is bromobenzene : water = 1·62 : 1. If M is the molecular weight of the bromobenzene,

$$\frac{\text{Bromobenzene}}{\text{Water}} = \frac{1 \cdot 62}{1} = \frac{M \times 119}{18 \times 641}.$$

Hence, $M = 157 \cdot 1$.

209. The Theory of Fractional Distillation.—It has already been stated that only one type of completely miscible mixture can be

separated into its components by fractional distillation, and this is the type which gives a vapour pressure curve possessing neither a maximum nor a minimum (§ 205). It is not, however, the vapour pressure-composition curve that is of so much interest for our present purpose, but the temperature-composition curve. This will, of course, be dependent upon the vapour pressure curve, but will not have the same form. If we plot the boiling point of a liquid against its composition we have a graph of the form ADB in Fig. 139.

But the composition of the vapour in equilibrium with the liquid at the boiling point is not the same as the composition of the liquid. It will contain more of the more volatile component. The curve ACB represents the variation of composition of the vapour with temperature.

Suppose we take a liquid containing about 60 per cent. A (point E on Fig. 139), and heat it until it boils. It will do this at a temperature F. The composition of the vapour in equilibrium with the liquid at this temperature is obtained by producing FD to the point G, where it cuts the vapour curve. On cooling this vapour, the composition of the distillate is H, which is obviously richer in B than the original liquid, since B is the more volatile liquid, having a lower boiling point. If the process is repeated, the temperature at which the distillate boils is J, and the vapour in equilibrium with it has a composition L, very closely pure B. In this way fractional distillation can be carried out. The corresponding curves for those liquids which give a minimum or a maximum in their vapour pressure curves are given below, and it will be seen that application of similar reasoning to the above indicates that separation is impossible.

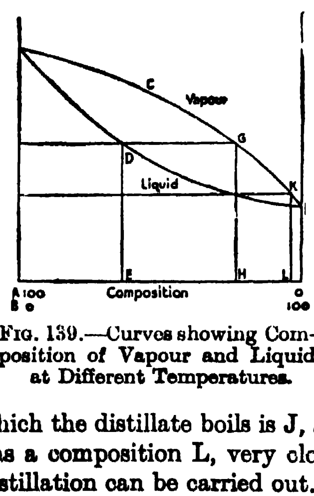
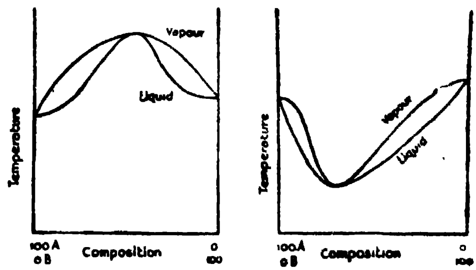


FIG. 139.—Curves showing Composition of Vapour and Liquid at Different Temperatures.

The efficiency of the process of fractional distillation is considerably improved by the use of a fractionating column, which consists of a long glass tube with a number of pear-shaped bulbs blown on it, or a tube packed with beads, so as to produce a large surface. This is attached to the neck of the distilling flask, and the vapour is made to traverse it before passing into the condenser. The vapour given off by the boiling liquid will be condensed in the column, and the vapour remaining over this condensed liquid will be very rich in the more volatile constituent of the vapour. If the condensed liquid is

obstructed in its return to the flask by a series of constrictions, such as the pear-shaped bulbs, an equilibrium is set up between the liquid and vapour at each constriction, and so the last amount of



Curve corresponding to (b), Fig. 135.

Curve corresponding to (c), Fig. 135.

FIG. 140.—Curves showing Composition of Vapour and Liquid at different Temperatures.

vapour to undergo condensation, at the top of the column, will be very rich in the more volatile constituent. The longer the tube, the better will be the separation.

E. SOLUTIONS OF SOLIDS IN LIQUIDS

210. General.—It is not possible to say with any certainty why a solid dissolves in a liquid. It is clear that the solubility or insolubility is not anything directly connected with the solute only, but that it is determined by both solute and solvent; for many substances which are insoluble in water will dissolve in other solvents, and *vice versâ*. The regular decrease in solubility with increase in atomic weight or atomic number in a family of elements, *e.g.*, calcium, strontium, barium and radium sulphates in water, indicates that solubility is connected with atomic number, and therefore with the number of extra-nuclear electrons in the metal atom, and the resultant electric field of the atom and molecule. There can be no doubt that solution depends upon the weakening of the electrical forces which ordinarily preserve the shape of the crystal lattice. As mentioned on p. 283, Tammann has shown that a crystal does not immediately break down on dissolution into molecules, but remains in "lattice blocks" of ultramicroscopic dimensions. These ultimately break up into molecules. The electrical properties of the solvent, then, must be such as to weaken these electrical crystal forces which are due to the electrical fields of the molecules themselves. The solution to the problem of why some substances dissolve in a certain solvent and others do not is to be found in a

study of the electrical properties of both solute and solvent, but our present knowledge is insufficient to enable us to give any definite answer.

The simplest external electrical property which can be measured, and can give any indication of the internal electrical field of a molecule, is the dielectric constant, and as far back as 1906 Walden suggested that the molecular solubility of a solute was related to the dielectric constant (e) by the expression

$$\frac{e}{\sqrt[3]{S}} = K,$$

where K is a constant and S is the molecular solubility of the solute expressed as a percentage, and given by the equation

$$S = \frac{100n}{n + N},$$

n and N being the numbers of gram-molecules of solute and solvent respectively in the solution.

It is clear that, according to this equation, liquids which have the higher dielectric constants should be the better solvents, and this is borne out in practice, as shown by the following data.

TABLE LXXVII.—SOLUBILITY OF POTASSIUM IODIDE IN VARIOUS SOLVENTS (Walden)

Solvent.	Formula	e.	Solubility, gms./100 gms. solvent. 25° C.
Water . . .	H_2O	81	59·54
Methyl alcohol. .	CH_3OH	35·4	14·97
Acetonitrile . .	CH_3CN	36·4	2·00
Ethyl alcohol . .	C_2H_5OH	26·8	1·92

However, numerous exceptions have since been discovered, and the Walden expression is no longer considered correct, but there is no doubt that dielectric constant, though not the only factor deciding solubility, must rank among the most important of these.

In dealing with organic bodies, it is frequently found that the substitution of one group or atom by another converts the substance from a soluble into an insoluble compound, and *vice versâ*. Thus, benzene is insoluble in water, but when one hydrogen atom is replaced by hydroxyl, the phenol produced is fairly soluble. The increased solubility is no doubt due to the affinity of the phenolic — OH group for water

It is interesting to note that whilst organic substances containing hydroxyl are nearly all soluble in water, inorganic hydroxides are nearly all insoluble.

211. Determination of Solubility.—The solubility of a substance is *the maximum weight of it which will dissolve in* 100 *gms. of the solvent at a given temperature.*

To determine this it is necessary to prepare a saturated solution of the solute and then analyse it.

It is easy to devise a suitable method where accuracy is not important. A saturated solution is prepared by shaking an excess of the solute with the solvent in a flask placed in a thermostat regulated to the required temperature. When the solution is saturated, some of it is removed by means of a pipette, provided with a plug of cotton wool or glass wool, to prevent any solid from being withdrawn. The solution withdrawn is placed in a dish of known weight and then weighed again. The solution is then evaporated to dryness and re-weighed. The difference between the weight of the dish alone and that of the dish and solid gives the weight of solute in the solution. The difference between the weight of the dish alone and that of the dish and solution gives the weight of the solution. The weight of solvent is the difference between the weight of solution and that of the solute. From these figures the solubility can be calculated.

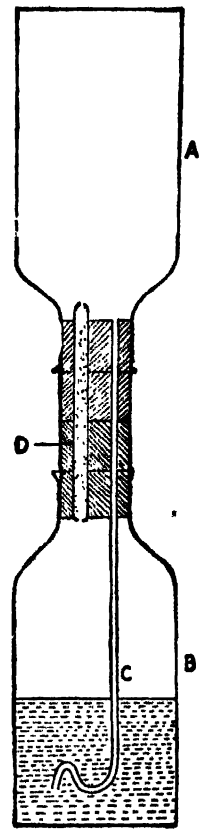


Fig. 141.—Apparatus for determining solubility.

It is clear that a number of errors are possible with this simple method. In the first place, the withdrawal involves a cooling, and some solid will be deposited in the pipette and may not be transferred to the dish. To overcome this, the pipette may be warmed in the thermostat before use. Also, the evaporation of a liquid to dryness is a highly undesirable operation to introduce into quantitative work, as it is so easy to lose liquid by spirting. This can be obviated by making use of some chemical method of analysis, where available.

An apparatus which has been used to determine the solubility of solids to a high degree of accuracy is shown in Fig. 141.

The apparatus is due to A. N. Campbell (*J. C. S.*, 1930, 179), and consists of two 1-oz. wide-mouth reagent bottles, A and B, provided with corks and arranged as shown. The mouth of A is ground. Glass tubes pass through the corks, D being a tube of about 3 mm. diameter, constricted at the upper end, and packed with glass wool, and C is a piece of quill tubing drawn out to a capillary and bent to an S shape, not, however, sealed off.

The bottle B is charged with solid and solvent, and fixed in the position shown in the diagram on the horizontal paddle of a thermostat stirrer. When solution is complete, the apparatus is inverted in the thermostat, and the solution filters through the plug, air coming into the top vessel, then B, through the capillary C. The liquid entering C at first is pure solvent, which will dilute the saturated solution when expelled by the air pressure from below, so it is advisable to have the tube as fine as possible. The very small amount of solvent contained by it will then be negligible, but in any case it will have a chance of becoming saturated before passing into the lower bottle, then A. The S bend in the tube prevents the admission of solid into A. When the solution has passed through, the apparatus is removed from the thermostat, and the weighed bottle A closed with a ground glass plate. The solution can then be analysed.

Where high temperatures are to be used, it is advisable to wire down the corks, as they may be forced out by the pressure.

For the determination of the solubility of sparingly soluble salts several methods are available. Most of these are fully dealt with in other sections. They can be summarised as :—

I. Electrical methods. (*a*) Determination of the solubility product by the E.M.F. method (see p. 648). (*b*) Determination of conductivity of the solution (see p. 512).

II. Colorimetric method. This depends on comparing the depth of colour of a solution with that of some standard solution. For example, to determine the solubility of lead sulphate, a quantity of it is shaken up with water, the solution filtered, and then hydrogen sulphide is passed through it to form lead sulphide. This is brown in colour : it will not be formed in sufficient quantity to give a definite precipitate, but the solution will be coloured brown through the presence of colloidal lead sulphide. The colour of this solution is compared with that obtained by passing hydrogen sulphide through a solution of lead acetate containing a very small, but known, lead ion concentration. The standard solution is progressively diluted, until the correct colour is reached, when the lead ion concentration in the unknown solution is obtained.

III. Radioactive method. The method of radioactive indicators

devised by Hevesy and Paneth finds some application in the determination of the solubility of sparingly soluble salts. A solution of a soluble salt of the metal of which the sparingly soluble substance is a salt is prepared, and a small known quantity of a radioactive substance is added. The sparingly soluble salt is then precipitated by the addition of the proper reagent, and it brings down with it the radioactive substance. It is filtered off, dried and weighed. A portion is then mixed with water in an ordinary solubility apparatus,

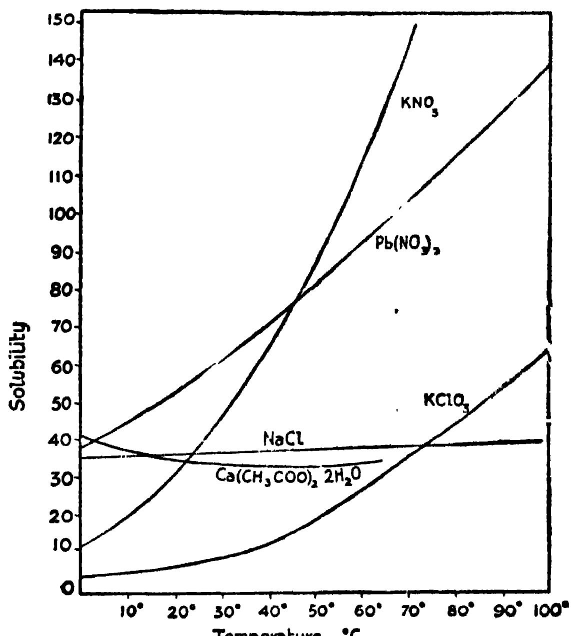


FIG. 142.—Solubility Curves.

such as that described above, and a saturated solution is prepared. A known volume of the solution is removed and evaporated to dryness, and the activity of the residue is determined by means of an electroscope. The activity is proportional to the amount of salt present, and, since a known amount of indicator was added to start with, the activity associated with a given weight of the salt is known, and the amount of substance present can be calculated. The method is very sensitive, and has afforded good results, particularly in the determination of lead and barium salts.

A satisfactory method for the rough determination of the solu-

bility of a sparingly soluble salt in the laboratory is to take a known weight of the salt and agitate it with one litre of water for some time at the temperature required. Filter off through a quantitative paper, and weigh the residue after drying. The difference in weight gives the amount dissolved by one litre of water.

212. The Solubility Curve and its Characteristics.—The solubility curve is the curve drawn between solubility and temperature. It may take a number of different forms. They may be considered in two sections: first, those which are continuous and, secondly, those which are discontinuous.

I. Continuous Solubility Curves.—A number of these are shown in Fig. 142.

As a rule, solubility increases considerably with the temperature. This is shown in the curves for lead nitrate and potassium chlorate (Fig. 142). Common salt is an outstanding case, the solubility increasing very little with temperature. A few substances are known, chiefly the calcium salts of organic acids, which decrease in solubility with increase in temperature. Examples are calcium acetate and calcium butyrate. Calcium sulphate has a peculiar solubility curve. Whilst continuous it shows a maximum, so that up to a certain temperature the solubility increases with temperature, and above that it decreases again.

The effect of temperature on the solubility of a substance which undergoes no chemical change with temperature can be predicted from a knowledge of its heat of solution. The heat of solution of most salts is negative, *i.e.*, heat is absorbed when the substance goes into solution. According to Le Chatelier's principle (§ 138), if the temperature of a saturated solution containing some of the solid salt is increased, a change will take place in the equilibrium to annul the effect of the increase in temperature, *i.e.*, that change will take place which absorbs heat Now the process that absorbs heat is the solution of the solid salt, and so more dissolves. If the heat of solution is positive, as it is in the case of many calcium salts of the fatty acids, then the reverse process will take place, for the dissolution of salt now involves absorption of heat.

On the basis of thermodynamics, it has been shown that the heat of solution and the solubilities of a substance at two given temperatures are connected by the equation

$$R \log_e \frac{s_1}{s_0} = H\left(\frac{1}{T_0} - \frac{1}{T_1}\right)$$

where T_0 and T_1 are the temperatures, on the absolute scale, s_0 and s_1 are the solubilities at these temperatures, R is the gas constant, and H the heat of solution. This equation, it will be noted, is

exactly similar to that given by Arrhenius for the effect of temperature on the rate of a reaction (p. 349).

This equation can readily be tested if the necessary data are given. Thus, at 0° C., the solubility of succinic acid in water is 2·88, whilst at 8·5° C. it is 4·22. Taking R as 2 gm.-cals. per degree, we have, substituting in the above equation,

$$2 \log \frac{4 \cdot 22}{2 \cdot 88} = H\left(\frac{1}{273} - \frac{1}{281 \cdot 5}\right),$$

$$H = 6{,}863 \text{ gm.-cals.}$$

The observed value for the heat of solution of succinic acid is 6,700 gm.-cals., agreeing very well with that calculated.

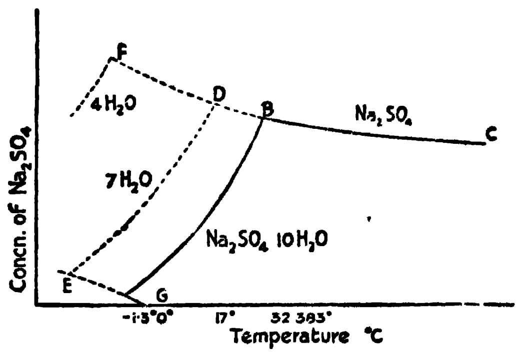


FIG. 143.—Solubility of Sodium Sulphate.

II Solubility Curve Discontinuous.—The solubility curve may, however, not be continuous, but may show sudden changes of direction. Whenever this occurs, it indicates that the solid phase in contact with the saturated solution has altered its character in some way, and that we really have to deal with two distinct solubility curves, which meet at a point. The temperature indicated by this point is that at which the transition from the one state to the other takes place. This alteration may be a polymorphic change or a change in hydration of the *solid* substance.

As an example of the effect of a polymorphic change on the solubility curve we may take ammonium nitrate. Within the range 10°–50° C., this substance changes its crystalline form. Actually this is only one of five such changes. When the solubility curve of this substance is plotted it is found to exhibit a distinct break at 32° C., the transition temperature of the β-rhombic into the γ-rhombic form (Fig. 107, p. 321). Another substance with a very similar solubility curve, showing a break due to polymorphic changes, is thallium picrate.

The other cause of breaks in the solubility curve, *viz.*, change in the degree of hydration of the solid in contact with the saturated solution, is considerably more common. One of the best examples is sodium sulphate (Fig. 143). If the solubility curve of sodium sulphate is plotted, it is found to have a very sharp break at 32·383° C., at atmospheric pressure. At this point there is an equilibrium in the solid state between the decahydrate, $Na_2SO_4.10H_2O$, and the anhydrous salt, so that below this temperature the solubility curve is that of sodium sulphate decahydrate, and above it it is that of anhydrous sodium sulphate. The curve CB can be followed backwards a short distance by seeding the saturated solution with the heptahydrate, so that the metastable portion BD is realised, and it is then possible to follow the solubility curve of the metastable heptahydrate DE.

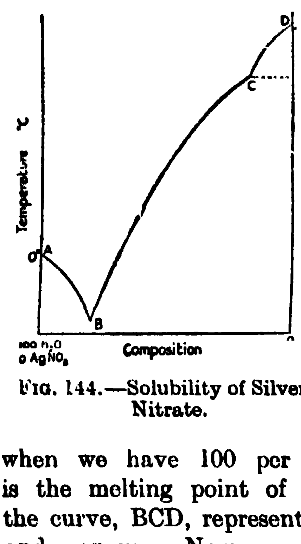


FIG. 144.—Solubility of Silver Nitrate.

Consider the complete solubility curve of a substance like silver nitrate. It is shown in Fig. 144. The solubility of this salt above 100° C. has been studied by Etard and by Tilden and Shenstone. The solubility increases with temperature, and there is a break in the solubility curve at 160° C., due to the formation of a new crystalline form. The curve continues until, when we have 100 per cent. silver nitrate, the temperature is the melting point of the salt, *viz.*, 208° C. This part of the curve, BCD, represents the equilibrium between salt, solution, and vapour. Now consider the other branch of the curve. Water freezes under atmospheric pressure at 0° C., but, if a small quantity of silver nitrate is added to the water, its freezing point is lowered, and the more salt added the lower is the freezing point. At last, however, a point is reached when the silver nitrate no longer dissolves, and is deposited along with the ice. At this temperature we have four phases, vapour, solution, salt, ice, all in equilibrium, and the system is therefore non-variant, as there are two components. The point B is thus a quadruple point. It may be regarded as the point of intersection of the solubility curve and the freezing-point curve. It is clear that this point B is the lowest temperature that can possibly figure on the solubility curve; it is the lowest temperature that can be attained with mixtures of two components in the presence of vapour. It is

usually called the *cryohydric point*, or the eutectic point (p. 393). It is clear that there is no distinction between solutions of water in liquid silver nitrate and of silver nitrate in water, in the right-hand limb of the curve.

For some time it was thought that the substance which was deposited at the cryohydric point was a definite chemical compound of the salt and water, and it was given the name *cryohydrate*. This, however, was disproved by Offer, who showed that although these substances appeared to be compounds, since they possessed a constant melting point, yet they were actually mixtures. This was shown by the fact that the heat of solution of the cryohydrate was the sum of the heats of solution of the ice and salt, in the proportion in which they are contained in the so-called "compound," and that similarly the specific volume of the cryohydrate was that calculated for a mixture. Also, the separate crystals of ice and salt can be distinctly seen, when the cryohydrate is examined under the microscope, particularly when the salt is coloured, *e.g.*, potassium permanganate.

This has an important bearing on the preparation of freezing mixtures. Until the cryohydrate separates we are dealing with a univariant system, and hence, if the temperature is varied, the composition of the phase in equilibrium will vary. Similarly, if the composition is varied, the temperature must alter. If ice is added to the univariant system salt—solution—vapour, the temperature must fall and the ice melt, and if enough ice is added the cryohydric temperature will ultimately be reached, provided that solid salt is added as fast as it dissolves. Similarly, if salt is added to the system ice—solution—vapour, the concentration of the salt will increase, ice will melt, and the temperature will fall, and again this will take place until the cryohydric temperature is reached, when the four phases can be in equilibrium.

In the preparation of freezing mixtures, both these methods can be used. In either case, there is an absorption of heat, and the temperature falls to the cryohydric point, which is the lowest temperature that can be attained. In practice, this temperature is very rarely reached owing to radiation, and absorption of heat by the solution formed. The latter can be counteracted by allowing the solution to drain off as soon as it is formed, and the former by increasing the rate of cooling, which can be brought about to a certain extent by rapid and intimate mixing of the components. Hence, it is better to use snow than ice in preparing a freezing mixture.

It is possible to have four phases present in a system of the type now under consideration, without ice being one of them This is so

where there is a change in the solid phase, as with sodium sulphate. Thus, at the point B in the solubility curve of sodium sulphate (Fig. 143), there are the phases anhydrous salt—hydrated salt—solution—vapour, and it is in fact a eutectic point, just as when one of the phases is ice. Where there is a possibility of the formation of a large number of hydrates before the salt melts, there are a number of these eutectic points in the solubility curve. This is well shown in the case of ferric chloride, the solubility curve of which is given in Fig. 145.

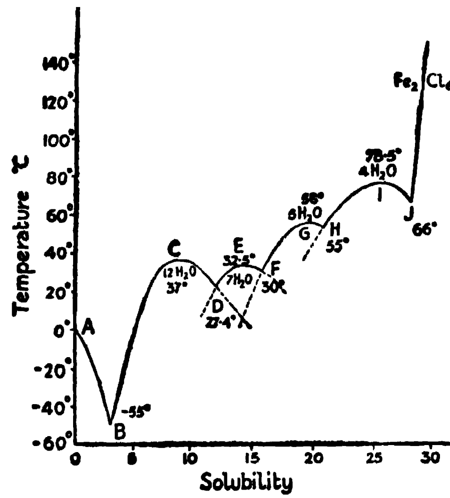


FIG. 145.—Solubility of Ferric Chloride Hydrates.

The curve AB shows the effect of adding ferric chloride to ice. It is, in fact, the freezing point curve of ferric chloride solutions, and B is the cryohydric point, $-55°$ C. If the solution is allowed to warm, and ferric chloride is added to keep the solution saturated, the curve BC is followed. This is the solubility curve of the dodecahydrate. At C this compound melts completely, and addition of anhydrous ferric chloride results in the formation of the compound $Fe_2Cl_6.7H_2O$. The solubility curve falls until the point D is reached, where there are again four phases, the dodecahydrate, $Fe_2Cl_6.12H_2O$, existing in equilibrium with the heptahydrate, $Fe_2Cl_6.7H_2O$. This is in reality, then, another eutectic point. If the solution is warmed, more ferric chloride will dissolve, and a similar curve is followed through E to F, the eutectic point for the hydrates $Fe_2Cl_6.7H_2O$ and $Fe_2Cl_6.5H_2O$. This goes on until

finally the curve is the solubility curve of anhydrous ferric chloride, ending at the melting point of the pure salt. Points such as C, G, E and I are called congruent melting points.

The various parts of this curve can be looked upon in a slightly different way. Starting from the point C, the curve CB represents the effect of adding water to $Fe_2Cl_6.12H_2O$, and therefore involves a lowering of the freezing point, whilst the curve CD represents the addition of ferric chloride to it, which again must lower the freezing point, so the curve drops away on both sides of the point C. Similar explanations can be given for the other humps.

It is clear that the number of these humps that can be detected on the solubility curve indicates the number of hydrates which are capable of existing in the solid state, and this therefore provides a valuable method of investigating hydrates. It must be clearly understood, however, that the solubility curve gives no evidence whatever as to the existence of hydrates in solution.

The dotted lines in the curve of solubility of ferric chloride represent metastable states that have been realised experimentally by taking the necessary precautions.

213. Supersaturation and Suspended Transformation.—The occurrence of a point such as B in the solubility curve of sodium sulphate (Fig. 143), or D, F, H, or J in the solubility curve of ferric chloride (Fig. 145), depends upon the co-existence of four phases. Sometimes the fourth phase does not appear, and consequently the point is not obtained. Thus, it is possible to follow the dotted lines in the two solubility curves just mentioned, since the fourth phase is not always formed. On cooling a solution of sodium sulphate from above the transition temperature, say 32·6° C., to room temperature, the hydrated form, $Na_2SO_4.10H_2O$, may not be produced at this temperature, so the solubility curve may be continued along the dotted line to D, and with great care even to F. It is thus possible to follow the solubility curve of a substance past the point at which it ceases to be the stable form. It is seen from the curves drawn that the solubility of the metastable form is greater than that of the stable form. This is analogous to the vapour pressures of stable and metastable states (§ 133). It is clear then that a solution of a metastable form must be more than saturated (supersaturated) with respect to the stable form. If the fourth phase is added to the solution in the form of a small crystal of the stable form, it follows that deposition of the stable form must take place until the concentration of the solution corresponds to the solubility of the stable form. It is therefore easy to bring about the deposition of the stable form from a solution containing the metastable form merely by adding a crystal of the phase required.

A similar case to this is the failure of some saturated solutions to deposit crystals when they are cooled beyond the point at which crystals would normally appear. This gives rise to supersaturated solutions. This behaviour is usually found with salts which crystallise with water of crystallisation. It is rarely found with anhydrous salts, though a good example of an anhydrous salt which easily forms a supersaturated solution is sodium chlorate.

The crystallisation of a solution which is supersaturated is readily brought about by the addition of a small crystal of the solute, or by the addition of dust particles or other nuclei about which crystallisation can take place. It is therefore a difficult matter to preserve a supersaturated solution in air, unless only air which has been filtered from dust particles is allowed to come into contact with the solution. Deposition of crystals from a supersaturated solution can also be brought about by mechanical disturbance, such as shaking, or rubbing the walls of the vessel with a glass rod (see also § 140).

214. Effect of Pressure on Solubility.—It is to be expected that solids which dissolve in a solvent with contraction of volume will have their solubility increased by the application of pressure, and that, conversely, substances which dissolve with increase in volume will have their solubility decreased by increase in pressure. This is a direct consequence of the principle of Le Chatelier (§ 138), and has been verified experimentally. Thus, when sodium chloride dissolves in water there is a contraction. At a pressure of 1 atmosphere the solubility at 18° C., expressed as the number of grams of salt in 100 gms. of solution, is 26·4. At a pressure of 500 atmospheres the solubility increases to 27·0.

215. Effect of Particle Size on Solubility.—When preparing a solution, the solute is usually powdered in order to increase the rate of solution. It is obvious that if the solvent can be in contact with a greater surface it will be able to dissolve the solid more quickly. In addition to assisting the rate of solubility, the particle size also makes a difference to the actual solubility. A saturated solution of calcium sulphate at 18° C. contains 2·085 gms. of the salt per litre when the particles are of ordinary size, but this increases to 2·476 gms. when the particles are reduced to a diameter of 0·3 μ (1 μ = 1 micron = 0·0001 cm.), about one-seventh of the ordinary size. The solubility of barium sulphate is almost doubled when the particle size is reduced from a diameter of 1·8 μ to 0·1 μ. This is clearly of importance in quantitative analysis. The more granular the precipitate the less will be lost in the washing processes.

The reason for this change in solubility lies in the increase in surface forces when the particles are smaller. It is well known that

the pressure inside a bubble is greater the smaller the bubble. In fact, the pressure is given by $2T/r$, where T is the surface tension and r the radius of the bubble, supposed formed inside a liquid. Now it must be supposed that similar forces to surface tension act at the surface of a solid. There is a great deal of evidence for this view based on adsorption and catalysis and other phenomena. If this is so, there must be a greater tendency for the smaller particle to expand, or to dissolve, since by that means it can reduce this internal pressure. Hence, it will be more soluble than the larger particles.

In the measurement of the E.M.F. of cells in which the electrodes are covered with a fine powder, the increased solubility of finely powdered substances has frequently been noted. If a cell is made up of two calomel electrodes, the electrode covered with the more finely powdered salt becomes positive to that covered with the coarse salt, owing to the difference in solubility (§ 277).

Reactions also proceed more rapidly when the reactants are finely powdered. This is probably due to increased surface forces.

216. Distribution of a Solid between two Non-miscible Solvents.—It has already been shown that in a system gas—liquid, the gas distributes itself in a definite ratio between the liquid itself and the space above the liquid, the concentration of the gas in the space above the liquid, divided by that of the gas in the liquid, being a constant. This is Henry's Law (§ 189). An identical law holds for the distribution of a solid or liquid between two liquids. When a liquid or solid distributes itself between two liquids, the ratio of the concentrations in the two liquid phases is constant, provided the substance dissolves in both solvents in the same form, *i.e.*, provided that no chemical combination takes place between the solute and either of the solvents, and that no association or dissociation takes place. Stated mathematically,

$$c/C = K,$$

where c is the concentration in one solvent and C that in the other. K is called the distribution coefficient, or partition coefficient. This is known as the *Distribution Law* (or sometimes the Partition Law) and is simply Henry's Law applied to solid or liquid instead of gas.

It is seldom found that the values of c/C are strictly constant through a series of determinations with different concentrations. The instances in which the ratio is reasonably constant over a considerable range which have been investigated include the distribution of hydrogen peroxide between water and some organic liquids, boric acid between amyl alcohol and water, iodine between water and chloroform, bromine between water and bromoform,

iodine between water and carbon disulphide, and phenol between water and amyl alcohol. It is not difficult to devise methods for analysing the phases in all these instances.

As with Henry's Law for gases, the Distribution Law does not hold where any change in the molecular condition of the distributed substance occurs when it dissolves in either solvent. The difficulty with liquid systems is that the corrections frequently have to be made in both liquids. The principle to be used is that the Distribution Law holds for those molecular species which are identical in the two solvents.

Consider first the instance where the substance *dissolves without dissociation in liquid A, but dissociates in liquid B.*

Let C_1 be the concentration of undissociated molecules in A, C_2 the total concentration in B, determined by analysis, and α the degree of dissociation. Then, by the ordinary law, the concentration of undissociated molecules in B must be $C_2(1-\alpha)$. Only the undissociated molecules can be in equilibrium, as there are no dissociation products in A to be in equilibrium with those in B.

Hence,
$$\frac{C_1}{C_2(1-\alpha)} = K.$$

If there is *dissociation in both liquids to different extents*, the problem becomes more complicated. Thus, let α_A be the degree of dissociation in liquid A, and α_B the degree of dissociation in liquid B. Let the concentration of the substance as determined by analysis (*i.e.*, total of undissociated and dissociated molecules) in liquid A be C_A, and in liquid B, C_B. Then, by the Law of Mass Action (§ 153), assuming the dissociation to take place into two components, we have

$$\frac{[\alpha_A C_A]^2}{(1-\alpha_A)C_A} = K_1 = \frac{C_A \alpha_A^2}{1-\alpha_A}.$$

Hence,
$$\alpha_A = \frac{-K_1 + \sqrt{K_1^2 + 4K_1C_A}}{2C_A} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similarly, for liquid B

$$\frac{[\alpha_B C_B]^2}{(1-\alpha_B)C_B} = K_2 = \frac{C_B \alpha_B^2}{1-\alpha_B}$$

and
$$\alpha_B = \frac{-K_2 + \sqrt{K_2^2 + 4K_2C_B}}{2C_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now, by Nernst's statement, the undissociated molecules in A will be in equilibrium with those in B. Hence,

$$\frac{C_A(1-\alpha_A)}{C_B(1-\alpha_B)} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting for α_A and α_B from (1) and (2), we have

$$\frac{C_A - \dfrac{\sqrt{K_1^2 + 4K_1C_A}}{2} + \dfrac{K_1}{2}}{C_B - \dfrac{\sqrt{K_2^2 + 4K_2C_B}}{2} + \dfrac{K_2}{2}} = K \quad . \quad . \quad . \quad . \quad (4)$$

or

$$\frac{2C_A + K_1 - \sqrt{K_1^2 + 4K_1C_A}}{2C_B + K_2 - \sqrt{K_2^2 + 4K_2C_B}} = K \quad . \quad . \quad . \quad . \quad (5)$$

We have two methods of testing this expression. Either we can work from equation (3) or from (5), according to the data at our disposal. If we know the degrees of dissociation we shall use equation (3). If we know the equilibrium constants we shall use (5).

Let us consider now the case of *association in one phase* and normal solution in the other. The reaction occurring may be represented as

$$X \rightleftharpoons nX \rightleftharpoons (X)_n.$$

If we analyse the phase in which normal solution has occurred, we shall obtain the concentration of the simple molecules in that phase (C_1), but if we analyse the other phase we find not only the concentration of single molecules, but also that of associated molecules. We have to find from this the concentration of single molecules only. Let the total concentration in this phase be C_2. By applying the Law of Mass Action to the equilibrium in this phase, we find, if α is the degree of dissociation of associated into simple molecules,

$$\frac{(C_2\alpha)^n}{C_2(1-\alpha)} = K_1; \; C_2\alpha = \sqrt[n]{K_1C_2(1-\alpha)}.$$

But $C_2\alpha$ is the concentration of simple molecules in the second phase, and hence the Distribution Law states

$$\frac{C_1}{C_2\alpha} = K = \frac{C_1}{\sqrt[n]{K_1C_2(1-\alpha)}}$$

whence we have the relationship

$$\frac{C_1}{\sqrt[n]{C_2(1-\alpha)}} = K'.$$

We can thus determine the degree of association in a solution. The above calculations apply whether the dissociation is of complex molecules into simpler ones (as supposed in the calculation), or if it is electrolytic.

It is easy to work out the other cases where we have combinations

of these already given. The results are given in tabular form below :—

Phase I C_1	Phase II C_2	Relationship
Normal . .	Normal . .	$K = \dfrac{C_1}{C_2}$
Normal . .	Association	$K = \dfrac{C_1}{\sqrt[n]{C_2(1 - \alpha)}}$
Dissociation .	Association	$K = \dfrac{C_1(1 - \alpha)}{\sqrt[n]{C_2\,(1 - \alpha')}}$
Normal . .	Dissociation	$K = \dfrac{C_1}{C_2(1 - \alpha)}$

It must be remembered that in all these cases we have assumed that the Law of Mass Action (§ 153) holds, and that the species distributed is the simple molecule.

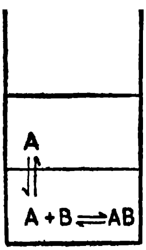


FIG. 146.

It is clear that the experimental study of the distribution of a substance between two liquids may prove instrumental in deciding whether it is associated or dissociated in any particular solvent and to what extent this change has taken place. In the case of electrolytic dissociation it is not so easy to use the method, since it is unusual to find a strong electrolyte which will also dissolve in a liquid which is not miscible with water.

Distribution may also be used in the study of other equilibria. Thus, the equilibrium constants of some reactions can be determined. Suppose we have a substance A, which will distribute itself between two solvents, and suppose that in the second solvent there is another substance, say B, with which A can form a compound AB. Suppose the upper layer contains z gms. of A. This is known by analysis. Let the bottom layer contain initially x gms. of A and y gms. of B. If the distribution coefficient is C, the bottom layer must contain Cz gms. of A, assuming the volume of both layers to be the same. Hence $x - z - Cz$ gms. of A must have combined to form AB. The weight of AB can thus be calculated, and the weight of free B deduced. This gives all the data required for calculating the equilibrium constant.

The use of the method in the determination of the degree of hydrolysis of salts is described on p. 564, in connection with the degree of hydrolysis of aniline hydrochloride. The theory of this experiment may be studied at this point.

The reaction between iodine and potassium iodide in the formation of I_3^- ions has been studied by investigating the distribution of

iodine between an organic solvent, such as chloroform, and an aqueous solution of potassium iodide. In a similar way, the existence of the Br_3^- ion in aqueous solution has been shown, and the hydrolysis of chlorine ($H_2O + Cl_2 \rightleftharpoons HCl + HOCl$) has also been studied. Dawson showed the existence of the compound $CuSO_4.4NH_3$ by investigating the distribution of ammonia between chloroform and aqueous solutions of copper sulphate.

Although this method can be widely used, it must be borne in mind that a knowledge of the equilibria occurring in each phase is necessary if trustworthy results are to be gained.

217. The Process of Extraction.—In organic chemistry, when it is necessary to separate a substance from a solution, recourse is frequently had to the process of extraction, in which the solution containing the substance required is shaken up with some solvent in which the required substance is more soluble, and the solutions separated. This is an example of the application of distribution.

It is frequently asked whether it is more economical to extract with all the liquid at one's disposal straight away, or to use it in several portions, separating each time. Thus, suppose we require to extract some succinic acid from aqueous solution with ether, and there is a given volume of ether at our disposal. Will it be more economical to use all the ether at once, or to use it in a number of portions?

This question can be answered by a simple calculation. Let W c.c. of a solution, containing x_0 gms. of substance, be extracted with A c.c. of a solvent. Let x_1 be the number of grams of unextracted substance. Then, the concentration of the substance in the extracting liquid will be

$$\frac{x_0 - x_1}{A},$$

and in the original solution

$$\frac{x_1}{W}.$$

Hence, by the Distribution Law,

$$K = \frac{\frac{x_1}{W}}{\frac{x_0 - x_1}{A}}.$$

$$\therefore\ x_1 = \frac{KW(x_0 - x_1)}{A} = x_0 \frac{KW}{KW + A}.$$

After a further extraction, with A c.c. of solvent, suppose that x_2 gms. remain in the original solution. Then,

$$x_2 = x_1 \frac{KW}{KW + A} = x_0 \left(\frac{KW}{KW + A}\right)^2.$$

After the nth extraction, the quantity unextracted will be

$$x_n = x_0 \left[\frac{KW}{KW + A}\right]^n.$$

If all the extracting liquid had been used at once,

$$\frac{\frac{x_n}{W}}{\frac{x_0 - x_n}{nA}} = K\ ;\ x_n = x_0 \frac{KW}{nA + KW}$$

and thus it is more economical to use it in portions. A numerical example will make this quite clear. An acid A is to be extracted from aqueous solution, in which it dissolves without dissociation, by means of ether. Fifty grams of the acid are dissolved in 1 litre of water. The distribution coefficient of the acid between ether and water is 3. One litre of ether is to be used in the extraction. Compare the amounts of acid left in the aqueous solution, (*a*) after extraction with the whole of the ether at once, and (*b*) after extraction with five portions of 200 c.c.

Case (*a*). *Extraction with all the ether at once.* Let x be the concentration in grams per litre in the ether layer. Then, by the Distribution Law,

$$\frac{x}{50 - x} = \frac{3}{1},$$
$$x = 37{\cdot}5.$$

Hence, the amount left will be 12·5 gms.

Case (*b*). *Extraction in five portions of* 200 *c.c.* Let x be the concentration in grams per litre in the ether layer in the first extraction. This time there are only 200 c.c. of ether, and so the actual weight extracted will be $x/5$ gms., leaving the concentration in the aqueous layer $(50 - x/5)$ gms. per litre. Hence, by the Distribution Law,

$$\frac{x}{50 - \frac{x}{5}} = \frac{3}{1},$$
$$x = 93{\cdot}75.$$

The amount extracted is thus 18·75 gms., leaving unextracted 31·25 gms.

Let x_1 be the concentration in grams per litre in the ether layer

in the second extraction. The weight extracted will be $x_1/5$ gms., leaving in the aqueous layer $\left(31{\cdot}25 - \frac{x_1}{5}\right)$ gms. per litre. Hence,

$$\frac{x_1}{31{\cdot}25 - \frac{x_1}{5}} = \frac{3}{1},$$

$$x_1 = 58{\cdot}6 \text{ gms.}$$

The amount extracted is 11·7 gms., leaving unextracted 19·55 gms.

In the third extraction, if x_2 is the concentration in grams per litre in the ether layer, by similar reasoning to the above,

$$\frac{x_2}{19{\cdot}55 - \frac{x_2}{5}} = \frac{3}{1},$$

$$x_2 = 36{\cdot}6 \text{ gms.}$$

The amount extracted is 7·3 gms., leaving unextracted 12·25 gms.

By similar calculation, the amount extracted in the fourth extraction is 4·52 gms., leaving unextracted 7·73 gms., and in the final extraction the amount extracted is 2·8 gms., leaving unextracted, as a result of the whole series of operations, 4·93 gms.

It is obvious from this calculation that it is considerably better to use the extracting solvent in small portions.

Using the formula

$$= x_o \left[\frac{KW}{KW + L}\right]^n,$$

we have, $x_o = 50$, $K = 0{\cdot}33$, $W = 1{,}000$, $L = 200$, $n = 5$. Hence,

$$x_n = 50 \left[\frac{333{\cdot}3}{533{\cdot}3}\right]^5,$$

$$= 4{\cdot}76 \text{ gms.}$$

This value differs slightly from that derived by taking all the steps separately, because in the former, approximations have been used in certain stages of the calculation.

In extraction from water, the greater the distribution coefficient, the more rapidly can the substance be extracted from the aqueous phase. It is frequently possible to increase the distribution coefficient artificially by making the substance less soluble in the aqueous phase. This can be done by adding some substance which depresses the electrolytic dissociation of the compound being extracted (§ 288). Thus, suppose that an organic acid, which ionises to a certain extent in aqueous solution, is to be extracted with

ether. If a strong inorganic acid is added to the solution, the hydrogen ion concentration is increased, and the ionisation of the organic acid is reduced. In the solution there will now be a greater amount of undissociated acid, and hence the amount extracted will be greater, the ionised acid not being extracted by ether. An organic base can best be extracted in the presence of a strong inorganic base. The addition of salts will also frequently lower the solubility of an organic compound in water (salting-out effect), and thus increase the distribution coefficient.

218. Recrystallisation.—A method of purification frequently adopted is to make use of the different solubilities of the pure substance and the impurity. The impure substance is dissolved in a solvent particularly chosen for the purpose, and then by lowering the temperature, or removing some of the solvent by evaporation, the less soluble, or more abundant, substance crystallises out. Suppose we have a substance containing an impurity. Enough solvent is added completely to dissolve the substance, and if too much is taken the solvent is evaporated until crystals appear. Or, the solvent may be added hot, and when it cools crystals will come down. Now, when crystals just appear, the solution will be saturated with respect to the pure substance, but not with respect to the impurity, for the concentration of this is much smaller. Consequently, the pure substance only crystallises out, until the solution becomes saturated with respect to the impurity. Of course, the crystals which are taken from the solution will contain a small amount of the mother liquor, which will be a concentrated solution containing the impurity, and so there is bound to be a small amount of impurity on, but not in, the crystals. This can be partly removed by careful drying of the crystals in a centrifugal machine, but a second or third recrystallisation is usually needed to give a satisfactory degree of purity.

There is always a loss of material when a purification is carried out by means of recrystallisation, for a time is reached when the solution is saturated with respect to both pure substance and impurity. Further separation cannot then be effected. The greater the difference in solubility of the two substances in the solvent chosen, the more efficient will the process be, for the amount of the less soluble substance (the substance required) present in a solution when it becomes saturated with the impurity will be smaller.

In manufacturing processes where recrystallisation is used, the process is not so simple as that outlined above. The temperature is carefully regulated, and various solvents are used by means of which more complete separation can be made.

F. SOLUTIONS OF SOLIDS IN SOLIDS

219. Solid Solutions.—When two substances are melted together, and the liquid cooled, it sometimes happens that instead of either component being deposited in the pure state, both substances are deposited at once. This is usually the case when substances are isomorphous. The solid thus deposited is called a solid solution; for, although a mixture, it is perfectly homogeneous, just as a solution of a solid in a liquid is homogeneous.

Solid solutions are most frequently met with in alloys. Thus, silver and gold, and cobalt and nickel, mix with each other in all proportions forming solid solutions.

When one metal dissolves in another, it lowers the melting point; just as, when a salt is dissolved in a solvent, the freezing point of the

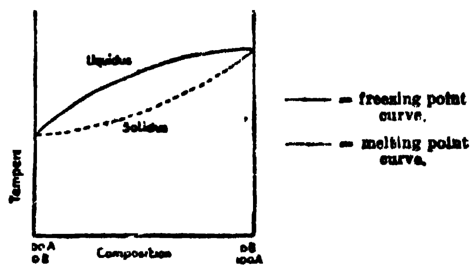


FIG. 147.

solvent is lowered. Thus, if tin is dissolved in lead, the melting point of the lead is lowered. When a solid solution is heated it begins to melt, but does not all melt at once. The melting point of a pure solid is sharp, whilst that of a solid solution is not sharp, the melting taking place over a range of temperature. Thus, the composition of the liquid produced when the solid solution melts is not, at first, the composition of the solid solution; only when melting is complete is this composition attained. The temperature at which solid begins to be deposited from the cooling liquid solution is usually called the freezing point of the mixture, and the temperature at which liquefaction just begins when the solid solution is heated is usually called the melting point. It is clear that there will be two temperature-composition curves of this system, showing (*a*) the composition of the liquid, and (*b*) the composition of the solid at any given temperature. The first is called the *liquidus*, and the second the *solidus* curve (Fig. 147).

This phenomenon is met with sometimes when determining the

melting point of an organic substance. Indeed, it is a usual method of recognising the presence of an impurity. If the substance is pure, the melting point is sharp; if impure, the substance melts over a range.

220. Freezing Point Curves of Solid Solutions.—There are three types of freezing point curve, just as there are three types of vapour pressure, or boiling point, curves for liquid solutions, already considered (p. 433). Indeed, the two cases are very similar.

The three freezing point composition curves are shown in Fig. 148.

In Curve I the freezing points of all mixtures lie between the

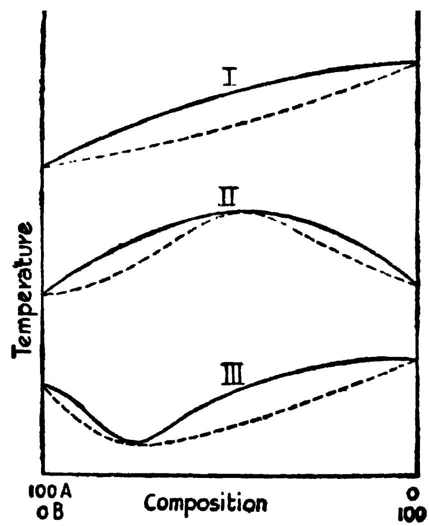


FIG. 148.

freezing points of the pure components. It is rather unusual for this type of curve to be found, for it indicates ideal solution, a phenomenon rarely met with in the case of liquids, and therefore likely to be more rare in the case of solid solutions. Examples of it, however, are the solid solution of β-naphthol in naphthalene, and that of anthracene in phenanthrene.

In Curve II the freezing point curve passes through a maximum. Again, few cases of this are known.

In Curve III the freezing point curve passes through a minimum, and this is the most common occurrence.

The dotted lines in Fig. 148 represent the melting point curves.

The curves given are the simplest types; more complicated cases

are usually observed, though they are modifications of the simple types.

221. **Fractional Crystallisation of Solid Solutions.**—Exactly similar considerations govern the fractional crystallisation of solid solutions as have been applied to the question of the fractional distillation of completely miscible liquid mixtures.

Consider the liquidus-solidus curve shown in Fig. 149. Each point on the continuous line AB represents the composition of the liquid in equilibrium with the solid, the composition of the latter, at any given temperature, being indicated by the corresponding point on the dotted line. In other words, the continuous line is the

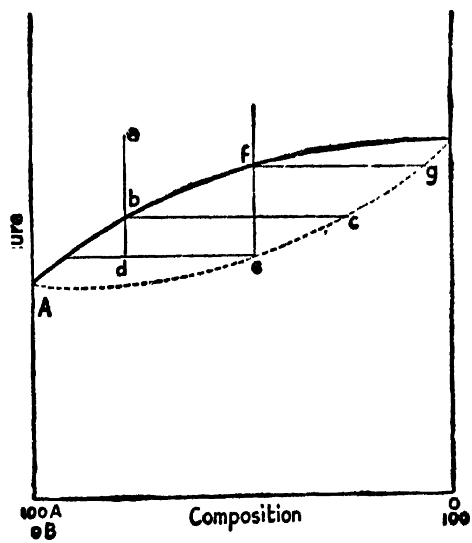


FIG. 149.

freezing point curve; the dotted line the melting point curve. The example given corresponds to Curve I in the previous section.

Consider a fused mixture of two substances, A and B, of the composition and temperature represented by the point *a*. This is cooled, and when it reaches the temperature represented by *b* a solid begins to separate, which will have the composition given by *c*. If, however, the mixture is allowed to cool to *d*, the solid separating has the composition given by *e*. Suppose the solid of this latter composition is removed from the system, and is then re-heated. It begins to melt at the temperature indicated by *e*, but is not entirely molten until a temperature given by the point *f* is reached. On cooling the liquid thus obtained, solid begins to form at the

temperature given by f, but its composition is g. It is to be noted that this solid is richer in B than the original. If the process is repeated, an almost complete separation into the two components can be effected. Theoretically, however, this would require an infinite number of operations, and so is impossible. It is possible, however, so to carry out the fractionation that the components are obtained as pure as is necessary.

As in the case of fractional distillation, it is impossible to effect complete separation when dealing with solid solutions for which the other types of freezing point-composition curve hold. A little consideration will show that if the freezing point curve has a maximum, fractional crystallisation will ultimately give a mixture having the composition corresponding to the maximum freezing point, and the liquid phase will get richer in the component which was in excess. If the freezing point curve has a minimum, the solid separating will be one of the pure components, whichever was taken in excess, and the liquid phase will approximate to the composition corresponding to the minimum freezing point.

SUMMARY

A solution is a perfectly homogeneous mixture.

A. Solutions of Gases in Gases.—Dalton's Law of Partial Pressures states that the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.

B. Solutions of Gases in Liquids.—The volume of gas absorbed by 1 c.c. of a liquid at any given temperature and pressure is the *solubility* of the gas. The volume of gas which would dissolve in 1 c.c. of the liquid if the pressure were 760 mm., and the temperature 0° C., is the *absorption coefficient* of the gas.

Gases are usually less soluble in salt solutions than in water. This may be due to the hydration of the salt, water being removed and unable to act as a solvent for the gas.

Gases are usually less soluble at higher than at lower temperatures. On heating a solution of a gas, the gas is usually expelled, but sometimes forms a constant boiling mixture (*e.g.*, HCl, HBr, etc.).

Henry's Law states that the mass of gas dissolved by a given volume of liquid at constant temperature is proportional to the pressure of the gas. The law may be stated in other ways: (*a*) the volume of gas absorbed is independent of the pressure, or (*b*) the concentrations of any single molecular species in two phases in equilibrium bear a constant ratio to each other at constant temperature.

Henry's Law is subject to deviations owing to non-ideality of the gases, compound formation, and dissociation or association of the gas in solution.

C. Solutions of Gases in Solids.—There are four types of solution: (*a*) formation of a perfectly homogeneous solution; (*b*) formation of two or more solid solutions; (*c*) formation of a chemical compound;

(*d*) adsorption, *i.e.*, taking up on the surface. To decide in which of these ways a solid has taken up a gas, the pressure-concentration diagrams may be studied.

D. Solutions of Liquids in Liquids.—The types occurring are illustrated by (*a*) phenol-water: giving an approximately parabolic solubility curve. At any temperature below 66·5° C., there are two phases; above it, the liquids are completely miscible. This temperature is called the critical solution temperature. (*b*) Triethylamine-water: below 18·5° C., the liquids are completely miscible; above it they are partially miscible, and two phases are formed. (*c*) Nicotine-water: below 60·8° C., and above 208° C., the liquids are completely miscible; between these two temperatures there is only partial miscibility. The vapour pressure curves of binary mixtures of completely miscible liquids fall into three classes: (*a*) the curve shows neither a maximum nor a minimum; (*b*) the curve shows a maximum; (*c*) the curve shows a minimum. Only with liquids giving a curve of type (*a*) can fractional distillation effect a separation of both the constituents.

E. Solutions of Solids in Liquids.—The solubility of a substance is the maximum weight of it which will dissolve in 100 gms. of the solvent at a given temperature. Breaks in the solubility curve indicate change of phase in contact with the solution, *e.g.*, change in hydration of a salt. Particle size influences solubility. The smaller the particle, the greater the solubility. A solid, which dissolves in two immiscible solvents, will distribute itself between them when shaken up with both together. The law governing the distribution is analogous to Henry's Law, and states that $c/C = K$, where c and C are the concentrations in the two liquids and K is a constant. Modifications of this law are necessitated by the occurrence of dissociation, association, or compound formation.

F. Solutions of Solids in Solids.—Solid solutions. The freezing point curves of binary mixtures are similar to the boiling point curves of binary liquid mixtures. Fractional crystallisation from a melt is analogous to the process of fractional distillation.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 25.—To study the system phenol-water.

Prepare sealed tubes containing the following amounts of phenol and water (approx.):—

	Phenol, gms.	Water, gms.
I	0·6	4·4
II	1·0	4·0
III	1·5	3·5
IV	2·0	3·0
V	2·5	2·5
VI	3·0	2·0

Take the first tube, place it in a beaker of water of which the temperature (observed) is gradually raised. Shake, and note the temperature when the turbidity suddenly disappears. Note also the temperature at which the two layers appear once more on cooling. Repeat these with the other tubes, taking in every case the mean of

the temperatures of appearance and disappearance of the turbidity as the temperature at which complete miscibility occurs. Plot the temperatures against the concentrations, expressed as percentages. The maximum of the curve is the critical solution temperature. (Theory, p. 429.)

Several other experiments in which Phase Rule principles are involved are suggested at the end of Chapter VII.

Experiment 26.—To determine the solubility of ammonia in water and in methyl alcohol.

Use the method described on p. 411. Generate the ammonia by warming the strong solution.

Experiment 27.—To determine the solubility of oxalic acid in water.

Adjust a thermostat for 25° C., and carry out the experiment as described on p. 441. Estimate the oxalic acid by means of standard permanganate. It is an interesting experiment to determine also the solubility of oxalic acid in N/10 sulphuric acid. Explain the result (Chapter XIII).

Experiment 28.—To determine the molecular weight of nitrobenzene by steam distillation.

Full instructions are given on p. 436. Instead of nitrobenzene, chlorobenzene may be used satisfactorily.

Experiment 29.—To verify the extraction formula with succinic acid and ether.

Try 200 c.c. ether, first all together, and then in five lots of 40 c.c., and see which is the more effective. The experiment is not altogether satisfactory owing to the solubility of ether in water.

The experiment may also be carried out with bromine water and carbon tetrachloride.

SUGGESTION FOR FURTHER READING

FINDLAY, A. "The Phase Rule and its Applications." (*Longmans*, 1927.)

QUESTIONS

(1) State Henry's Law. How far does it explain accurately the equilibrium between a gas and a solvent ?

(2) How would you attempt to verify Dalton's Law of Partial Pressures ? How may this law be deduced on the basis of the kinetic theory ?

(3) Discuss the absorption of hydrogen by palladium.

(4) What are the characteristics of the solubility curves of (*a*) sodium sulphate in water, (*b*) phenol in water, (*c*) nicotine in water ?

(5) Give the theory of fractional distillation.

(6) How may the molecular weight of a substance volatile in steam be obtained from a steam distillation experiment ? What are the conditions that this experiment should give an accurate result ?

(7) Deduce the general equation for extraction of a solid from solution by means of a liquid immiscible with the original solvent, with n extractions of v c.c. each.

(8) How would you distinguish between a solid solution and a solid chemical compound ?

(9) In a recent investigation of the system anthracene-phenanthrene, Bradley and Marsh (*J. C. S.*, 1933, 650) obtained the following data :—

Per cent. anthracene by wt.			0·56	2·30	3·13	5·06	5·82	9·54	11·7	13·3
Per cent. phenanthrene by wt.			99·44	97·70	96·87	94·94	94·18	90·46	88·3	86·7
F.p., ° C. . . .			98·3	101·2	102·6	106·2	106·8	114·8	119·2	120·2
M.p., ° C. . . .			97·8	99·2	100·0	101·4	102·0	105·0	107·2	107·6
Per cent. anthracene by wt. .	20·5	27·1	28·9	36·4	44·4	58·5	72·3	81·2	94·3	100·0
Per cent. Phenanthrene by wt.	79·5	72·9	71·1	63·4	55·6	41·5	27·7	18·8	5·68	0·00
F.p., ° C. .	134·0	145·4	147·8	159·4	170·0	186·4	199·2	204·8	213·2	218·0
M.p., ° C. .	113·5	118·2	120·8	126·2	133·2	147·8	170·0	182·2	207·6	218·0

Draw the liquidus-solidus curves, and discuss them. Also, find the melting point of pure phenanthrene.

CHAPTER XI

DILUTE SOLUTIONS

222. Perfect Solutions.—In this chapter we shall deal with those properties of solutions which are common to all solutions, and the effect on these of altering the composition of the solution. Such properties are called *colligative properties*.

Strictly speaking, these properties are none of them common to all solutions, but only to those solutions which are ideal, or perfect. It will be found that errors such as those encountered when dealing with gases prevent the perfect applicability of the laws discovered. *A perfect solution is one for which the volume change accompanying a small dilution is additive.* Thus, if we have 100 c.c. of a solution, and add 10 c.c. of water to it, the total volume would be 110 c.c. if the solution were perfect. This, however, does not hold for any solution. There is always a slight deviation. The more dilute a solution is the more nearly does it approach ideality. That is why we shall deal in this chapter with dilute solutions only. The laws then discussed will be applicable to all dilute solutions to a close approximation; but if we include strong solutions the laws no longer hold, because these are far from being perfect.

223. Methods of Expressing Concentrations of Solutions.—The properties to be dealt with in this chapter are determined rather by the numbers of molecules present than by the actual weights of the substances present. The method of expressing the concentration of a solution by means of the weight dissolved in a given volume, *i.e.*, grams per litre, although it could be used, would be unnecessarily complicated. The best method is to express the concentration in gram-molecules per litre. Frequently the method of "mol-fractions" is used. If n_a is the number of gram-mols. of the substance a, and n_b that of the substance b contained in a given solution, then the mol-fraction of a is $N_a = \dfrac{n_a}{n_a + n_b}$, and of b, $N_b = \dfrac{n_b}{n_a + n_b}$.

224. Osmosis.—If a strong solution of copper sulphate is placed at the bottom of a tall cylindrical vessel, and is then carefully covered with water, so that the heavier solution is not disturbed, the two layers are, at first, more or less well defined. After some

months, however, the two solutions are found to have formed a mixture, in which the two layers can no longer be discerned. This happens even though convection currents (which could cause mixture) are completely prevented by keeping the apparatus at a constant temperature throughout the experiment.

Some force must be acting upon the molecules of copper sulphate in the strong solution to cause them to become distributed throughout the liquid. This force is known as *osmotic pressure*. The movement of molecules of solute goes on until the concentration throughout the solution is the same. The osmotic pressure is therefore a function of the concentration. If two solutions of different concentrations are brought into contact, the system is not in equilibrium. The osmotic pressure causes the molecules of the solute in the stronger solution to be transferred to the weaker solution until the osmotic pressures are equalised, when equilibrium is attained.

The process may be looked upon in the reverse way. The strong solution gradually becomes more dilute, so that the existence of osmotic pressure causes the progressive dilution of the solution by the entrance of water. It is clear that if a strong solution of copper sulphate is placed in a vessel closed with a membrane through which water, but not the molecules of copper sulphate, can pass—a semi-permeable membrane—the copper sulphate solution will gradually get more dilute, water entering the vessel.

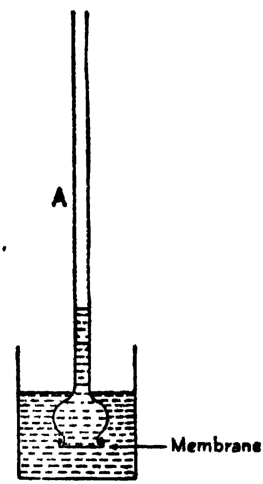


FIG. 150.—Apparatus to demonstrate the Existence of Osmotic Pressure.

The phenomenon of osmosis was first observed by the Abbé Nollet, who closed the end of a tube with an animal membrane, and filled the tube with sugar solution. The tube was then placed in a beaker of water. The water entered through the membrane, diluted the sugar solution, and rose in the tube. The experiment is easily carried out with the apparatus shown in Fig. 150. The thistle funnel A has a membrane (pig's bladder) tied over the end. It is then filled with sugar solution and placed in a beaker of distilled water. The water rises in the stem of the thistle funnel until the hydrostatic pressure equalises the pressure driving the water in. This pressure is the osmotic pressure, and is measured by the height to which the solution will rise in the tube.

The osmotic pressure is caused by the force which tends to bring about equilibrium between the pure solvent and the solution.

The first quantitative experiments on osmotic pressure were carried out with an apparatus like the above, using pig's bladder as the membrane. Traube showed that inorganic substances would also act as membranes, for instance, copper ferrocyanide, $Cu_2[Fe(CN)_6]$, precipitated when potassium ferrocyanide solution is added to copper sulphate solution. It is necessary for a membrane of this sort to be supported in some way, and this was accomplished by producing the substance in the walls of a porous pot. It is a matter of great difficulty to get a porous pot suitable for the work. The pores must all be the same size, as otherwise certain parts of the pot have to bear more pressure than others, and the membrane is ruptured at that spot.

Osmotic pressure is of great importance in physiological processes. The cell-walls are semi-permeable membranes, *i.e.*, they allow some substances to go through, *e.g.*, water, but not others, *e.g.*, salt, in just the same way as the pig's bladder.

If a cell containing a solution of a definite osmotic pressure be placed in a solution of less osmotic pressure, water will enter the cell in an attempt to equalise the concentrations and bring about equilibrium. The cell will swell. If, however, the reverse is the case, the cell solution having the smaller osmotic pressure, water will leave the cell and it will shrink. If it is placed in a solution of the same osmotic pressure, water neither enters nor leaves the cell, and it remains the same size. Solutions having the same osmotic pressure are called *isotonic solutions.*

225. The Experimental Determination of Osmotic Pressure.—(*a*) *The Method of Pfeffer.*—A special porous pot was taken, and prepared to take the membrane in the following way: the pot was first treated with a dilute solution of potassium hydroxide, and then with a 3 per cent. solution of potassium nitrate, after which it was washed out and dried. It was then filled with water, and the water forced into the pores by pressure. It was afterwards placed in a 3 per cent. solution of copper sulphate for some time to allow the salt to get well into the pores, and a solution of the same salt was placed inside the pot. The interior of the pot was washed out and quickly dried. The cell was then allowed to stand in air until the outside was just wet, when it was filled with a 3 per cent. solution of potassium ferrocyanide and again placed in the copper sulphate. After this, the cell was tested for various pressures.

In carrying out an experiment, the cell was filled with a solution, usually sugar, of which the osmotic pressure was required. A mercury manometer was fixed to the cell, and the whole was placed

in water kept at a constant temperature in a large tank. Water entered the cell, and the pressure attained was measured by the manometer.

(b) *The Method of Morse and Frazer.*—Morse and Frazer improved upon Pfeffer's method in several details, although the general procedure was the same. The chief innovation was the deposition of the copper ferrocyanide membrane electrolytically, a more even deposit being thus obtained. The cell was filled with a M/10 solution of copper sulphate, and placed in a vessel containing M/10 potassium ferrocyanide, platinum electrodes being placed in both solutions. The electrodes were connected to a battery, and the copper ions were driven out of the pot, whilst ferrocyanide ions

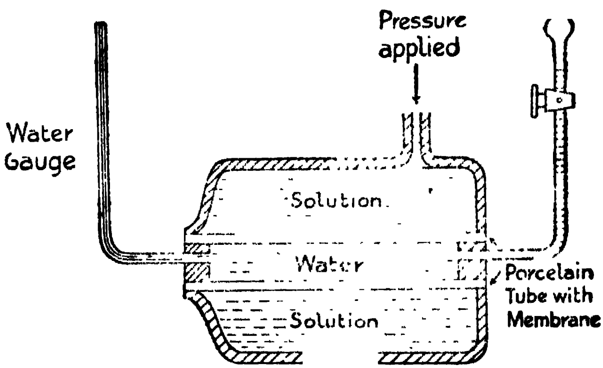


FIG. 151.—The Apparatus of Berkeley and Hartley (diagrammatic).

were drawn into it. Where they met, somewhere in the wall of the pot, they combined and formed the membrane.

Morse and Frazer also used great care in choosing the correct pots for high pressure work. The results obtained by these observers are the usually accepted ones. They determined the osmotic pressure of cane-sugar solutions up to 91 per cent. strength, the strongest solution giving an osmotic pressure of 273 atmospheres.

(c) *The Method of Berkeley and Hartley.*—An important change in method was used by the Earl of Berkeley and E. G. Hartley. Instead of measuring the osmotic pressure directly, they measured the force necessary to prevent the entrance of liquid into the pot, so what they actually did was to counterbalance the osmotic pressure by an external pressure, the value of the latter giving the value of the osmotic pressure. The apparatus is represented diagrammatically in Fig. 151.

The results of the method agree with those of Morse and Frazer.

The same investigators have also used a dynamic method of measuring the osmotic pressure, by determining the rate of flow of solvent into the solution.

(*d*) *Methods of Comparing Osmotic Pressures.*—As has already been mentioned, the cells of plants and animals have walls composed of semi-permeable materials through which water can pass. De Vries applied this fact to the determination of relative osmotic pressures by placing cells in the two solutions to be compared and noting how much each had to be diluted in order to give a solution of which the osmotic pressure was the same as that inside the cell.

Tammann has used an ingenious method based on the detection of the currents produced when one liquid flows into another of different density. When no currents were observed, the solutions were isotonic.

226. The Laws of Osmotic Pressure.—The following is a table of the results of Berkeley and Hartley's determination of the osmotic pressure of sucrose solutions at 0° C. In the last column, the pressure (*P*) has been multiplied by the volume containing one gram-molecule of the sucrose (*V*).

TABLE LXXVIII.—OSMOTIC PRESSURES OF SUCROSE SOLUTIONS (Berkeley and Hartley)

Concentration.	Osmotic Pressure, *P*.	Volume containing 1 gram-mol., *V*.	*PV*.
	Atm.	Litres.	
2·02 gm./litre	0·134	169·3	22·7
10·0 ,,	0·66	34·2	22·6
20·0 ,,	1·32	17·1	22·6
45·0 ,,	2·97	7·60	22·6
93·75 ,,	6·18	3·65	22·5

It is at once seen that the product *PV* is constant, a relationship recalling the behaviour of a gas, and corresponding to Boyle's Law.

Since the product of the osmotic pressure and the volume containing one gram-molecule of solute is constant, the osmotic pressure divided by the concentration must be a constant. Thus, osmotic pressure is directly proportional to the concentration.

It is clear that Boyle's Law may be applied to dilute solutions if the pressure used in the equation is the osmotic pressure developed, and the concentration is the reciprocal of the volume containing a given weight of the solute.

It is remarkable that the effect of temperature on osmotic pressure is also similar to the effect of temperature on the pressure of a gas. The pressure is proportional to the absolute temperature. The table below shows the variation of the osmotic pressure of sucrose solutions with temperature according to observations by Morse and Frazer.

TABLE LXXIX.—EFFECT OF TEMPERATURE ON OSMOTIC PRESSURE OF SUCROSE SOLUTIONS

t, °C	T, ° Abs	Osmotic Pressure, P.	P/T.
0	273	7·085	0·02594
10	283	7·334	0·02591
20	293	7·605	0·02595
25	298	7·729	0·02594

As the osmotic pressure of a solution is both proportional to the concentration, and to the absolute temperature, an expression such as

$$PV = KT$$

must govern the combined effect of these variables. K is a constant.

Using the data that have been obtained experimentally, the value of K may be calculated. Taking the data for the concentration of 10 gm./litre, we see from Table LXXVIII that the value of the osmotic pressure is 0·66 atmos. The volume containing one gram-molecule is 34·2 litres, and the temperature is 0 °C., *i.e.*, 273° Abs.

Inserting these in the equation, we have

$$PV = KT,$$

$$0{\cdot}66 \times 34{\cdot}2 = K \times 273,$$

$$K = \frac{0{\cdot}66 \times 34{\cdot}2}{273} = 0{\cdot}0824 \text{ litre-atmos. per degree.}$$

This is in good agreement with the gas constant R, which on the same system of units is 0·0821 litre-atmos. per degree (§ 76).

There are, then, clearly marked relationships between osmotic pressure and gas pressure. The same laws govern both. This can be put into a statement as follows : *The osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature, and occupying the same volume as the solution.*

The first to note this relationship was van't Hoff, making use of Pfeffer's observations. Whilst this law is true for non-electrolytes,

such as sugar and other organic substances, it does not hold for electrolytes, which give higher values for the osmotic pressure than required by this theory. The reasons for the deviation of electrolytes from the laws of dilute solutions will be taken up in greater detail later (§ 256).

227. Determination of Molecular Weights of Substances in Solution by means of Osmotic Pressure.—Since we know that osmotic pressure is related to the volume of a solution containing one gram-molecule of a substance by the relationship

$$PV = 0{\cdot}0821\ T$$

when P is measured in atmospheres, V in litres, and T in degrees Absolute, it is clear that if we measure P and T we can find V.

To determine the molecular weight of a substance in solution by the osmotic pressure method, the osmotic pressure of a solution of the substance of known strength is determined at a definite temperature. Inserting the values of P and T in the above equation, the volume of solution containing one gram-molecule of the solute is obtained. Since the weight of solute dissolved in a given volume of solvent is known, the molecular weight is easily calculated.

The method is not frequently employed owing to the great difficulties attendant upon osmotic pressure measurement.

228. Numerical Examples.—Some numerical examples will make the method of calculation quite clear.

(1) Ten grams of a substance were dissolved in 250 c.c. of water, and the osmotic pressure of the solution was found to be 600 mm. of mercury at 15° C. Find the molecular weight of the substance.

Let M be the molecular weight of the substance. Then 10 gms. correspond to $\frac{10}{M}$ gram-molecules. This is dissolved in 250 c.c. of water. Hence, 1 gram-molecule is dissolved in $25M$ c.c. $= 0{\cdot}025\ M$ litres. This is V. $P = 600$ mm. $= \frac{600}{760}$ atmos. $T = 288°$ Abs. Substituting these values in the equation, we have

$$PV = 0{\cdot}0821\ T,$$

$$\frac{60}{76} \cdot 0{\cdot}025M = 0{\cdot}0821 \times 288,$$

$$\therefore M = \frac{76 \times 0{\cdot}0821 \times 288}{60 \times 0{\cdot}025},$$

$$= 1197{\cdot}6.$$

(2) A substance of molecular weight 286 was used in an osmotic pressure experiment. A solution containing 10·3 gms. of the

substance in 100 c.c. of water was made up. What osmotic pressure should the solution exert at 20° C. ?

Let P be the osmotic pressure. From the data given,

$$V = \frac{28 \cdot 6}{10 \cdot 3} \text{ litres.}$$

$$T = 293^{\circ} \text{ Abs.}$$

Substituting in the equation

$$PV = RT$$

$$P \times \frac{28 \cdot 6}{10 \cdot 3} = 0 \cdot 0821 \times 293,$$

$$P = \frac{10 \cdot 3 \times 0 \cdot 0821 \times 293}{28 \cdot 6} \text{ atmos.}$$

$$= 8 \cdot 662 \text{ atmos.}$$

229. Theories of Osmotic Pressure and Semi-permeability.—Whilst the facts of osmotic pressure and the laws governing it are known, we are still a long way from knowing the cause of this phenomenon. Several theories have been put forward, none of which provides a perfectly satisfactory explanation, and it seems that until a more thorough theory of the liquid state is developed a correct theory of osmotic pressure and of semi-permeability will not be possible.

Traube considered the semi-permeable membrane as being a sort of molecular sieve, which would allow small molecules of the solvent to pass through, but which stopped the progress of the larger solute molecules. This theory was of course only applicable to certain cases, for examples are known where the molecule of the solute must be smaller than that of the solvent, and yet the membrane still acts as a semi-permeable one.

Another theory which was put forward by Bigelow assumes that the membrane acts like a set of very fine capillary tubes, and that the process of semi-permeability is intimately connected with capillarity.

Armstrong proposed a chemical theory whereby the solvent was supposed to form a kind of loose chemical compound with the membrane, and was later split off again. There is little evidence for the truth of this view.

The theory of preferential solubility, which states that one of the substances, in this case the solvent, dissolves in the membrane, diffuses through it, and is given off again at the other side, seems to be the most generally applicable. It is supported by the experiment already quoted (§ 182) in connection with the proof of Dalton's Law of Partial Pressures, in which the hydrogen in a mixture of

nitrogen and hydrogen is separated by passing the mixture through a heated palladium box. Without going into great detail, we may say that the hydrogen dissolves in the palladium, diffuses through it, and is given off again at the other side. This gives quite a reasonable picture of what might be happening in osmosis through a semi-permeable membrane.

Nevertheless, the theory of semi-permeability is not of such great importance as that of osmotic pressure. Osmotic pressure would be developed whether there were any semi-permeable membrane there or not. The membrane is merely used in order to enable the pressure to be measured. The theory of osmotic pressure itself is quite independent of any theory of semi-permeability. The latter cannot in any way affect it, and the truth or untruth of any statement concerning the membrane does not alter the facts of osmotic pressure.

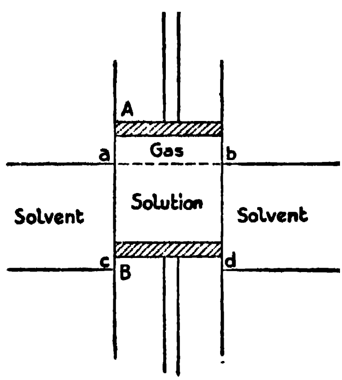


FIG. 152.

There are two outstanding theories of osmosis. The first is the kinetic theory, in which osmotic pressure, like gas pressure, is supposed to be due to the bombardment of the molecules of solute on the membrane. The number of collisions of the solvent with the wall will be less on the side of the solution than on that of the solvent, and the latter therefore flows through in an attempt to make the number equal.

The other theory is the hydrostatic theory. The entrance of solvent into the solution is supposed to be due to the existence of an attractive force of the solvent for the solute. This might be due to variation of surface tension.

It may be pointed out that the osmotic pressure is not developed at the surface of a liquid. Ordinary bottles of reagents contain liquids of which the osmotic pressure may be measured in hundreds of atmospheres. Yet the bottles do not burst. A consideration of surface tension shows that the liquid itself is under considerable pressure, and, indeed, liquids are known to possess internal pressures of great magnitude.

230. Thermodynamic Proof of the Identity of the Gas and Osmotic Pressure Laws.—This proof was originally due to Rayleigh, though it is usually associated with the name of van't Hoff. Consider a

reversible cyclic process (§ 314), carried out at a temperature $T°$ Abs.

Suppose that we have a gas at pressure p in equilibrium with its solution of osmotic pressure P. ab is a semi-permeable membrane allowing gas to pass through, but not liquid, and ac and bd, the wall of the cylinder, is also semi-permeable, allowing the solvent, but not the gas, to pass through. The pistons, A and B, are not permeable.

Stage I.—Move the pistons A and B up, so that a volume v equal to the volume occupied by one gram-molecule of the gas at pressure p is transferred through the membrane ab from the solution to the gas side. A will move up through a volume v, but B moves up through a volume V, which is equal to the volume of solution in which one gram-molecule is dissolved.

The amount of solvent corresponding to the volume of solution transferred passes through the wall ac and bd. The maximum amount of work done in the movement of the upper piston is pv, and in that of the lower PV. In the former the work is done *by* the system, in the latter *on* the system. Hence, the net work done is $pv - PV$.

Stage II.—The volume of gas, thus passed through, must be restored to the solution by a reversible and isothermal path in order to obtain the maximum amount of work. This is accomplished in this and the succeeding two stages.

The volume v of gas separated from the system is allowed to expand isothermally and reversibly to a practically infinite volume. The maximum work done in this process is

$$\int_v^{v_\infty} pdv = \int_v^{v_\infty} \frac{RT}{v}. dv = RT \log_e \frac{v_\infty}{v}.$$

Stage III.—The gas is now brought into contact with a volume V of the solvent. It dissolves infinitely slowly, because it is infinitely dilute. If, however, the gas is gradually compressed with a frictionless piston, it will dissolve. Let p_1 be the pressure applied. Then the work done on the system is

$$-\int_0^{v_\infty} p_1 dv_1.$$

To evaluate the integral, we must consider the question as follows: When one gram-molecule of gas has dissolved the pressure on the piston must be equal to p, so, assuming the accuracy of Henry's Law, $\frac{p_1}{p}$ gram-molecules will dissolve at pressure p_1, leaving $1 - \frac{p_1}{p}$ gram-molecules undissolved.

$$\therefore p_1 v_1 = \left(1 - \frac{p_1}{p}\right) RT,$$

$$\therefore p_1 = \frac{RT}{v + v_1},$$

$$\therefore - \int_{v_1 = 0}^{v_1 = v_\infty} p_1 dv_1 = - RT \left[\log_e (v + v_1) \right]_{v_1 = 0}^{v_1 = v_\infty}$$

$$= - RT \log_e v_\infty$$

since v is negligible compared with v_∞.

Stage IV.—This volume of solution must be returned to the original solution, a process which involves no work. Since we are here dealing with an isothermal and reversible cycle, the total amount of work done in it must be equal to zero. Hence,

$$pv - PV + RT \log \frac{v_\infty}{v} - RT \log \frac{v_\infty}{v} = 0,$$

$$\therefore pv = PV.$$

By the gas laws

$$pv = RT.$$

Hence,

$$PV = RT,$$

so that osmotic pressure obeys the gas laws.

231. Raoult's Law of Vapour Pressure Lowering.—It has been known for some time that a solution of a salt boils at a higher temperature than the pure solvent. This means, of course, that the vapour pressure of a solution is less than that of the pure solvent. Gay-Lussac was amongst the first to investigate this lowering of vapour pressure, and he found that the vapour pressure of a solution of sodium chloride, of specific gravity 1·096, was 0·9 of that of pure water. He failed, however, to discover any law underlying the phenomenon.

Von Babo (1848–49) carried out numerous experiments on the vapour pressure of salt solutions, but discovered only that the lowering of vapour pressure and the concentration of the salt were connected by a complicated geometrical series. The work was taken up by Wüllner, in 1856, who was the first to discover the simple law at the basis of this phenomenon. He used aqueous solutions and came to the conclusion that "the diminution of the vapour pressure of water caused by substances dissolved therein, which substances do not themselves exert any noticeable pressure at the temperature of the experiment, is proportional to the quantity of the substance in the solution."

In 1887, Raoult extended the work to cover other solvents besides

water, and discovered the connection between the lowering of vapour pressure and the molecular weights of the solute and solvent. He stated that "the lowerings of vapour pressures of solutions in different solvents are equal when the proportion of the number of molecules of the dissolved substance to the number of molecules of the solvent is the same." Raoult used twelve different solvents, and dissolved many substances in them, finding the relative lowering of vapour pressure for one molecule of each substance in 100 molecules of solvent. This was constant.

Combining the statement of Wüllner with that of Raoult, it may be said that *the vapour pressure of a solution is proportional to the mol-fraction of the solvent present in the solution* (§ 223). This is Raoult's Law of Vapour Pressure Lowering.

Suppose that the mol-fraction of solvent in a solution is n_s, then that of the solute must be $1 - n_s$. Let p_s be the vapour pressure of the solution. Raoult's Law states that

$$p_s = kn_s \qquad (1)$$

where k is a constant.

If p_o is the vapour pressure of the pure solvent,

$$p_o = k \qquad (2)$$

since, in the pure solvent, $n_s = 1$.

Hence, from equations (1) and (2),

$$p_s = p_o n_s \qquad (3)$$

Now, from equations (1) and (3), a more convenient mathematical expression of Raoult's Law may be derived. We have

$$\frac{p_o - p_s}{p_o} = 1 - n_s$$

$$= 1 - \frac{\text{number of molecules of solvent}}{\text{total number of molecules in solution}}.$$

$$\therefore \frac{p_o - p_s}{p_o} = \frac{n}{N + n}$$

where n is the number of molecules of solute, and N is the number of molecules of solvent.

The law holds only for perfect solutions; indeed, one method of defining a perfect solution is that of Hildebrand, who states that it is a solution which obey's Raoult's Law. For other solutions deviations of a serious nature occur. If we are dealing with perfect solutions, we may plot the vapour pressure against the composition, and shall obtain curves of the type shown in Fig. 153. The vapour pressures of the two components are additive (Dalton's Law, § 181), so that a straight line CD is obtained upon which the total vapour pressure of the solution will lie. When a solid is dissolved in a

liquid, the vapour pressure of the solid is extremely small, and hence the vapour pressure of the mixture will be practically that of the solvent. This is shown in Fig. 153.

The vapour pressure curves of mixtures of two liquids have already been dealt with (§ 205). It will be remembered that these were of three distinct types, (*a*) a straight line (or a line showing neither a maximum nor a minimum), (*b*) a curve showing a maximum, and (*c*) a curve showing a minimum. Raoult's Law would hold for liquid mixtures, if such mixtures were perfect solutions (§ 222). Actually, only those mixtures which give the straight line vapour pressure curve obey Raoult's Law. The existence of maxima and minima in the curves indicates that Raoult's Law is not being obeyed. The deviations from the law may be due to association,

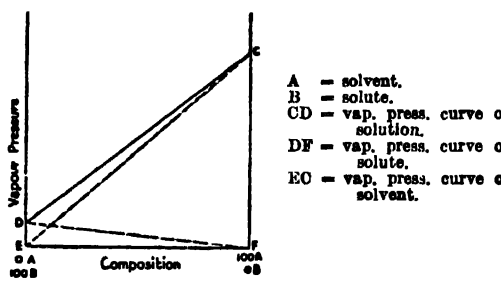


FIG. 153.—Vapour Pressure-composition Curves for Solutions. The curves refer to one particular temperature.

in which case it may be shown that a maximum in the vapour pressure curve is to be expected. A minimum is found when compound formation takes place between the solute and solvent, though this is not always the explanation. When electrolytic dissociation (§ 251) occurs, Raoult's Law can still be applied if, instead of *n*, the number of molecules of solute, the number of ions is substituted.

In the case of solutions of solid non-electrolytes, Raoult's Law is of more or less general application. A solid contributes a negligible amount to the total vapour pressure, whereas, with liquids, the vapour pressures of the two components are of the same order, and deviations will be more marked.

232. Derivation of Raoult's Law.—Raoult's Law may be derived theoretically from the Distribution Law (§ 216). Consider the distribution of molecules of the vapour between the gaseous and liquid phases. Let N be the number of molecules of pure solvent, and n the number of molecules of solute added. The molar concen-

tration of the solvent before the solution is made is $\frac{N}{N}$ $(= 1)$; afterwards it is $\frac{N}{N+n}$.

Let C_0 be the concentration of molecules in the gaseous phase over the pure solvent, and C the concentration of gas molecules over the solution. By the Distribution Law, the ratio of the concentrations of the same molecular species in the gaseous and liquid phases is constant. Hence,

$$\frac{C_0}{\frac{N}{N}} = \frac{C}{\frac{N}{N+n}} = K,$$

$$\therefore \frac{C_0}{C} = \frac{N+n}{N},$$

$$\therefore \frac{C_0 - C}{C_0} = \frac{n}{N+n}.$$

Since the concentrations of molecules in the gaseous phase are proportional to the pressure,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{N+n},$$

where p_0 is the vapour pressure of the solvent, and p_s that of the solution. This is the mathematical expression of Raoult's Law.

233. Connection between Vapour Pressure Lowering and Osmotic Pressure.—As has been already stated, there is a definite connection between osmotic pressure and all the other colligative properties of solutions. It is the purpose of this section to derive the mathematical relationship between the osmotic pressure and the vapour pressure of a solution.

There are several methods of doing this, but the simplest is that given below.

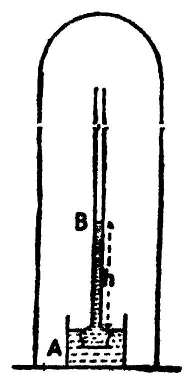


FIG. 154.

Consider a tube, closed by a semi-permeable membrane and containing a solution, immersed in a vessel containing the pure solvent. The whole arrangement is placed under a bell-jar, which is evacuated. The osmotic pressure of the solution is measured by the height h, to which the liquid rises in the tube.

Consider the vapour pressure of the solution at B, calling it p'. This must be equal to the pressure of the vapour of the solvent at B, otherwise there would be a distillation process taking place at B. If

the vapour pressure of the solution were less than that of the solvent at B, some of the solvent would condense on the solution, which would become more dilute until the vapour pressures were equalised. Conversely, if the vapour pressure of the solution were greater than that of the solvent at B, distillation would go on from the solution, and more solvent would be drawn through the membrane. In either case there would be a continuous flow of liquid up or down the tube, and equilibrium would not be established.

Now what is the vapour pressure of the solvent at B? It will be different from that at the surface of the liquid by an amount equal to the pressure of a column of the vapour of height h. Thus, if p is the vapour pressure of the pure solvent,

$$p - p' = hd,$$

where d is the density of the vapour.

We now have to find the density of the vapour. Let the molecular weight of the solvent be M. The volume occupied by M gms. of vapour at pressure p and at temperature T is

$$V = \frac{RT}{p}.$$

The density of the vapour is, then,

$$d = \frac{M}{V} = \frac{Mp}{RT}.$$

Assuming that the density of the dilute solution is equal to that of the solvent s, the osmotic pressure P is given by

$$P = hs.$$

Hence,

$$p - p' = \frac{P}{s} \cdot \frac{Mp}{RT}, \text{ or } \frac{p - p'}{p} = \frac{MP}{sRT}.$$

We can derive Raoult's equation from this statement as follows: If V' is the volume of solvent containing one gram-molecule of the solute,

$$P = n\frac{RT}{V'}.$$

But

$$V' = \frac{NM}{s}, \text{ where } N = \text{number of gram-mols. of solvent.}$$

Hence,

$$P = \frac{nsRT}{NM}.$$

Substituting in the equation above, we have

$$\frac{p - p'}{p} = \frac{M}{s \,.\, RT} \cdot \frac{nsRT}{NM} = \frac{n}{N}.$$

which is a modified form of Raoult's Law, in which n, which is small compared with N, since the solution is dilute, is neglected in the denominator.

234. Use of Raoult's Law in the Determination of Molecular Weights.—It is clear that if the lowering of the vapour pressure of a solvent brought about by dissolving a known weight of solute in a given weight of the solvent is known, its molecular concentration can be determined. Knowing the weight of substance and the volume of solvent in which it is dissolved, it is then an easy matter to calculate the molecular weight.

235. Numerical Examples.—Some examples will make this clear.

(1) The vapour pressure of water is 92 mm., at 50° C. 18·1 gms. of urea are dissolved in 100 gms. of water, and reduce the vapour pressure by 5 mm. Calculate the molecular weight of urea.

The number of gram-molecules of water present is 100/18. That of urea is $18{\cdot}1/M$, where M is the required molecular weight. Raoult's Law states

$$\frac{p_o - p_s}{p_o} = \frac{n}{N + n}.$$

Substituting the values

$$p_o - p_s = 5 \text{ mm.}, \; n = \frac{18{\cdot}1}{M},$$

$$p_o = 92 \text{ mm.}, \; N = \frac{100}{18},$$

we have
$$\frac{5}{92} = \frac{\frac{18{\cdot}1}{M}}{\frac{100}{18} + \frac{18{\cdot}1}{M}}.$$

Inverting,
$$\frac{92}{5} = \frac{\frac{100}{18} + \frac{18{\cdot}1}{M}}{\frac{18{\cdot}1}{M}} = \frac{100\,M}{18 \times 18{\cdot}1} + 1,$$

$$\therefore M = \frac{\frac{92}{5} - 1}{100} \times 18 \times 18{\cdot}1 = \frac{17{\cdot}4 \times 18 \times 18{\cdot}1}{100},$$
$$= 56{\cdot}7.$$

The molecular weight is 56·7.

(2) At 20° C. the vapour pressure of ether is 442 mm. of mercury. When 6·1 gms. of a substance were dissolved in 50 gms. of ether, the vapour pressure fell to 410 mm. What is the molecular weight of this substance?

$$\text{Here } p_o = 442 \text{ mm.} \quad n = \frac{6{\cdot}1}{M},$$

$$p_s = 410 \text{ mm.} \quad N = \frac{50}{74},$$

since the molecular weight of ether is 74.

Substituting in the equation

$$\frac{p_s - p_s}{p_s} = \frac{n}{N + n},$$

$$\frac{32}{442} = \frac{\frac{6{\cdot}1}{M}}{\frac{50}{74} + \frac{6{\cdot}1}{M}},$$

$$\therefore \frac{442}{32} = \frac{50M}{6{\cdot}1 \times 74} + 1,$$

$$\therefore M = 115{\cdot}7.$$

The molecular weight is 115·7.

236. Experimental Determination of Vapour Pressures.—There are two types of experiments by means of which vapour pressures may be determined. The first is static, and the second dynamic in nature. In the static methods the pressure itself is directly measured. In the dynamic methods the vapour pressure is obtained by measuring some effect due to it (see also § 92).

The static method was first used by von Babo in 1848, and later by Wüllner (1856), whose work paved the way for the generalisation of Raoult. Raoult himself determined vapour pressures by the static method, preparing first a barometer with a Torricellian vacuum over the mercury, and introducing the substance, of which the vapour pressure was required, over the mercury. The depression of the mercury level, owing to the vapour pressure of the liquid, was measured. This was a direct measure of the vapour pressure. By comparing the amounts of depression caused by the pure solvent in one barometer tube, and the solution in another, the lowering could readily be obtained.

Dieterici used a differential method for measuring the vapour pressure. The method depends on the determination of the difference of vapour pressure of solvent and solution. He used a glass plate connected to a quartz thread to which was attached a mirror. The glass plate was arranged so that the difference of pressure caused a movement of the plate (Fig. 156). This movement was used to twist the quartz thread, which moved the mirror. A beam of light reflected from the mirror would be deflected through twice the angle the mirror turned through. The sensitivity of the apparatus was very great, and Dieterici claimed to observe a pressure difference to an accuracy of 0·001 mm.

A similar idea to this was used by Lord Rayleigh in the con-

struction of the differential manometer. A diagram of this is given in Fig. 155. The two limbs, X, Y, were filled with mercury. The height of the mercury in each limb was dependent upon the pressure to which each was connected. The forked manometer was tilted until the two ivory pointers, BB, just touched the level of the mercury. The angle through which the mirror M was deflected was measured by the deflection of a beam of light reflected from it. As before, the deflection of the reflected beam was twice the angle the mirror had been turned through.

This manometer was applied by Frazer and Lovelace in their experiments on the depression of vapour pressure. They obtained

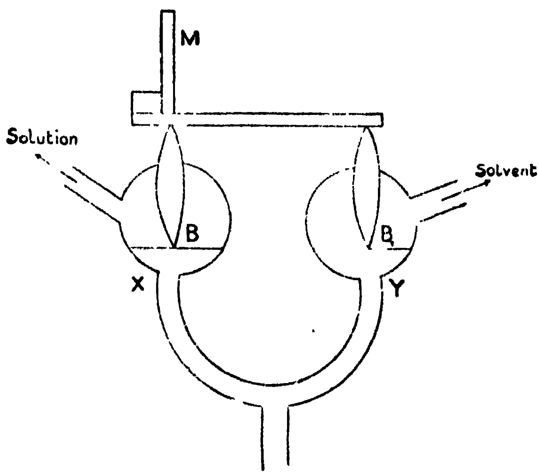


FIG. 155.—Lord Rayleigh's Differential Manometer.

very accurate results for a number of solutes. For a description of their apparatus the student is referred to H. S. Taylor's "Treatise on Physical Chemistry" (Macmillan, 1924), pp. 260-261.

All methods of determining vapour pressures demand that the temperature be kept constant, and this must be carefully remembered, as a slight change in temperature may alter the vapour pressure considerably.

The dynamic methods have been more extensively applied than the static ones, as they are easier to use, and can be made to yield quite accurate results.

The principle of Ostwald and Walker's dynamic method (1888) is as follows: A known volume of air is passed through the solution, and then through the pure solvent. In the first case it becomes saturated up to the vapour pressure of the solution, and the solution

loses weight proportionally, the loss being determined by weighing before and after the air has passed through. In the second case the air takes up a little more vapour, since the vapour pressure of the solvent is greater than that of the solution. The loss of weight of the solvent is proportional to the difference in vapour pressures of the solution and the solvent.

When the solvent is water the vapour pressure of the solvent is best obtained by passing the air, after it has been through solution and solvent, through calcium chloride tubes, which will catch all the water, and which by weighing before and after the experiment will give the total weight of water in the air, which is proportional to the vapour pressure of the solvent.

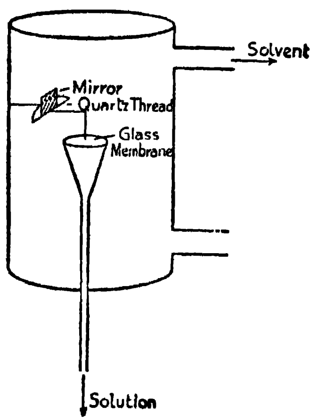


FIG. 156.—Dieterici's Apparatus.

The apparatus required for this method is shown in Fig. 157. A are three wash-bottles in which is placed the solution. Then follow B, three wash-bottles containing pure solvent. These are followed by three calcium chloride tubes. It is only necessary to weigh the wash-bottles containing the solvent before and after the experiment, and the calcium chloride tubes. The difference of weight of the former is proportional to the difference in vapour pressure $(p_0 - p_s)$, and that of the latter to the vapour pressure of the solvent (p_0). We thus have $\frac{p_0 - p_s}{p_0}$.

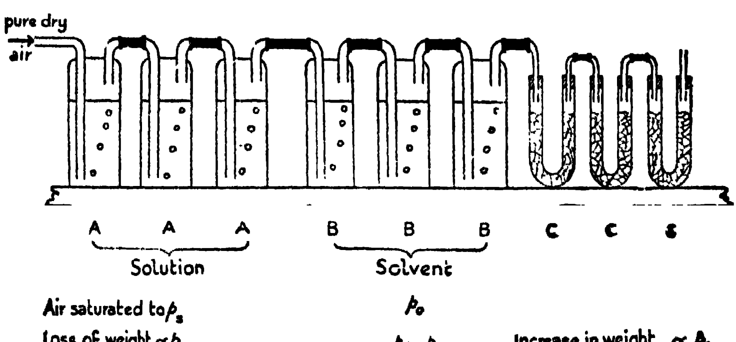


FIG. 157.—Apparatus for Ostwald and Walker's Dynamic Method.

Walker applied this method to the investigation of aqueous solutions, and Will and Bredig (1889) used it for alcoholic solutions. It is obvious, when the effect of the electrolytic dissociation of salts in aqueous solution on the colligative properties is considered (§ 256), that all the methods of determining molecular weights in solution based on these properties will be of much more value for organic than for inorganic substances. Many organic substances are insoluble in water but soluble in alcohol, and hence Will and Bredig's

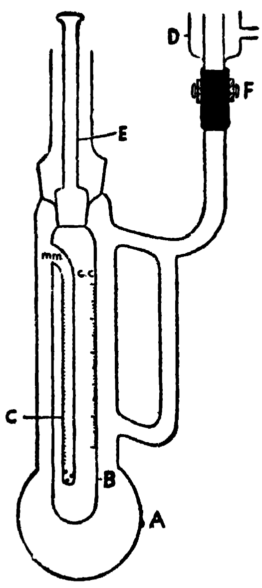


FIG. 158.—Menzies' Apparatus.

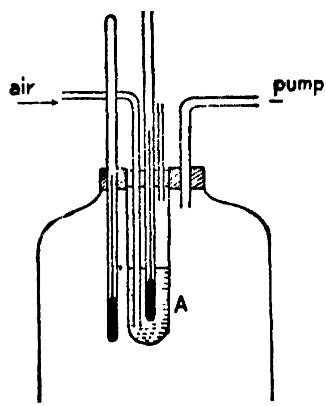


FIG. 159.—Apparatus for Cumming's Dew-point Method.

modification of the Walker method was of considerable use. Instead of absorbing the vapour of the solvent, the loss in weight of both sets of bulbs was obtained. The current of air was maintained for twenty-four hours, the flow being about 1 litre per hour.

In Menzies' method, the difference in pressure at which a pure solvent and the solution boil at the same temperature is determined. The apparatus is shown in Fig. 158. The bulb A contains the solvent, whilst the inner tube B contains the solution. This tube is provided with a scale graduated in c.c. The further inner tube C has a millimetre scale. It is first necessary to determine the zero point. This is done by connecting up the condenser D, and then half

filling A with the solvent. The liquid is boiled vigorously for a few minutes to boil out any dissolved gas, and the inner vessel B is filled with the boiled-out liquid. When the liquid in the outer vessel is boiling steadily, the stopper E is removed, and the screw-clip F is partly closed. Vapour will blow through the solvent in B. After a minute or two, the stopper is replaced loosely, and when it has warmed up it is fully inserted and the clip F opened. The liquid is kept boiling steadily. In about five minutes the level in the inner tube will have become stationary, and a little higher than that in the surrounding vessel, owing to capillarity.

A weighed tablet of the substance to be dissolved is now added to B, and the blowing through repeated. The solution having a lower vapour pressure than the solvent, the level of the liquid in the inner tube will come to rest lower than that in the tube it surrounds. The difference of the reading of the level of the liquid in the tube C, for the solution and for the pure solvent gives the lowering of the vapour pressure in terms of millimetres of solution. The density of the solution must be known, or may be taken for rough purposes as equal to that of the solvent. The concentration of the solution is known from the reading of the volume of the solution in the inner tube.

The dew-point method of Cumming is of interest, though not often applied. It depends upon the fact that a liquid begins to be deposited from the vapour state when the vapour is saturated. Thus dew forms from damp air when the temperature is such that the air is saturated. From a knowledge of the degree of cooling required for the deposition of dew, the vapour pressure can be determined. The apparatus is shown in Fig. 159. A silver tube A, containing ether and bearing a thermometer graduated to 0·1° C., and an exit and a delivery tube, is held in a cork so that its lower end is inside a bottle containing the solution. This bottle is first exhausted, and then air is blown through the ether, causing it to cool owing to rapid evaporation. This cools the vapour in the neighbourhood. The temperature at which dew begins to form is noted, and the tube is then allowed to warm up and the temperature at which the dew disappears is noted. This is repeated several times, and the mean of the results taken. This gives the dew-point. The vapour pressure of the solvent at this temperature (found from tables) is the vapour pressure of the solution at the temperature of the vapour.

237. Elevation of the Boiling Point.—Since, as has already been shown, when a solute is dissolved in a solvent, the vapour pressure of the solution is less than that of the pure solvent, it follows that the boiling point of the solution must be higher than that of the

pure solvent. This point is easily seen when the vapour pressure curves of the solvent and the solution are considered (Fig. 160). The curves AB and CD represent the variation of vapour pressure of the solvent and solution respectively with temperature. The boiling point is the temperature at which the vapour pressure of the liquid is equal to the superimposed pressure. Let P represent the superimposed pressure. Then T and T_1 will represent the boiling points of the pure solvent and the solution respectively. It is obvious that T_1 is greater than T. If, then, we measure the boiling point of a solution, we should be able to discover the molecular weight of the solute. Indeed, the determination of the boiling point of the solution under atmospheric pressure is only another way of determining its vapour pressure.

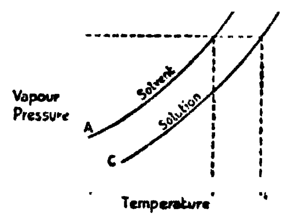


FIG. 160.—Vapour Pressure-temperature Curves for the Solvent and Solution.

It is usually much more convenient to determine a boiling point than to determine a vapour pressure, so the determination of the elevation of the boiling point is an exceedingly important method of determining molecular weights in solution.

It follows from Raoult's Law (§ 231) that equimolecular weights of different substances will increase the boiling point of a solvent by the same amount, since they depress the vapour pressure by the same amount. The elevation of the boiling point of a solvent caused by the solution of one gram-molecule of any substance in, say, 100 gms. of it, will therefore be a constant for that solvent. The values of these constants for the solvents most frequently used are given in the Table below.

Suppose that a solution is made of *w* gms. of a solvent, and *W* gms. of solute of unknown molecular weight *M*. Let the elevation

TABLE LXXX.—MOLECULAR ELEVATION (per 100 gms. solvent).

Solvent.	*K*. °C.	*K* calc. $\frac{0{\cdot}02T^2}{L}$. °C.
Water . . .	5·2°	5·15°
Chloroform . . .	38·8°	38·0°
Ether	21·1°	20·9°
Acetone . . .	17·2°	17·2°
Benzene . . .	25·7°	26·1°
Ethyl alcohol . .	11·5°	11·9°

of the boiling point be $T°$ C. Now, one gram-molecular weight of any substance, dissolved in 100 gms. of the solvent, raises the boiling point by the same amount, $K°$ C. In the solution under consideration there are W gms. of solute dissolved in w gms. of solvent. In 100 gms. of solvent there would be $\frac{100W}{w}$ gms. of solute. This raises the boiling point $T°$ C. The weight which will raise the boiling point by $K°$ C. is the molecular weight. Hence, $M = \frac{100WK}{wT}$

The value of K is sometimes given for the elevation of the boiling point produced when one gram-molecule of a solute is dissolved in 1,000 gms. of solvent (instead of 100 gms. as given in the above Table). These values would be one-tenth of those given above.

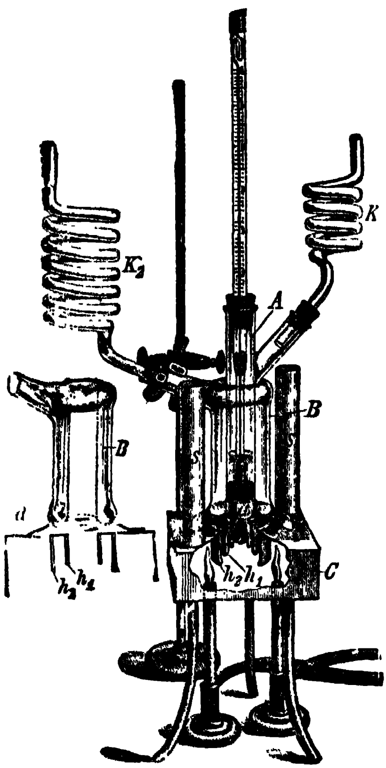


FIG. 161.—Beckmann's Boiling-point Apparatus.
[*By permission of Messrs. Baird and Tatlock (London) Ltd.*]

238. Experimental Determination of Elevation of the Boiling Point.—(*a*) *Beckmann's Method.*—The method of Beckmann is the oldest of the methods used. It has been improved upon in several ways, to be described later.

The apparatus is shown in Fig. 161. A weighed amount of the pure solvent, say 25 gms., is boiled in the boiling tube A, which has a piece of platinum wire sealed through the bottom, and may also be partly filled with glass beads or garnets. The purpose of these is to prevent superheating, which is the chief source of error in the method. The point of the wire, and the beads, help to break up the bubbles of vapour, and thus prevent any superheating. This boiling tube is provided with a coiled air condenser which returns the liquid to the tube as it vaporises. If this were not used, the strength of the solution would vary throughout the determination, and no result could be obtained.

The tube is not heated directly, but is surrounded by a heating vessel B, in which some of the same solvent is boiled. This, too, is provided with a reflux condenser, the object in this case being merely to avoid waste of the liquid. The whole apparatus is heated on an asbestos box C, which is provided with chimneys, *s*, *s*, for promotion of currents. The boiling tube itself rests on two asbestos rings, h_1 and h_2. The whole purpose of this is to prevent any direct heating by the flame in order to avoid superheating.

Having determined the boiling point of the pure solvent, a weighed pellet of the substance under examination is dropped into the liquid through the side tube, and the tube is again heated. The boiling point is again found. The experiment may be repeated by the addition of a fresh pellet of the substance, and noting the further rise in the boiling point.

To obtain accurate results with liquids for which the molecular elevation is small, it is necessary to use a very sensitive thermometer. Such an instrument was devised by Beckmann for this purpose. It does not read the absolute boiling points of the liquids, but merely the difference in temperature of the boiling points of the pure solvent and of the solution. This is all that is required in the calculation. It consists of a large bulb connected to a very fine capillary tube, with a bulb at the top which can accommodate excess mercury. If the thermometer is required for measuring comparatively low boiling points, it is necessary to get most of the mercury up into the top reservoir and detach it from the main thread. In this way the mercury may be made to appear on the scale at any desired temperature. This operation is known as "setting" the Beckmann thermometer. For further details, the practical text-books should be consulted.

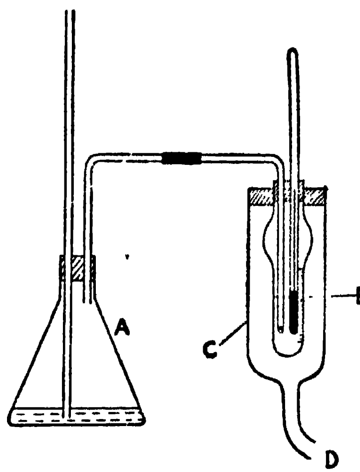


FIG. 162.—Apparatus for the Landsberger Boiling-point Method. (The small hole at the top of B cannot be shown in the figure.)

In more modern forms of the apparatus, electrical methods of heating are used.

(*b*) *The Landsberger Method.*—This differs from Beckmann's method in that the solution is heated to the boiling point by passing into it the vapour of the pure solvent. Since, when the latter

condenses, it gives up its latent heat, the liquid may be boiled by this means. The advantage of this process is that there is no danger of superheating.

The apparatus is shown in Fig. 162.

The conical flask A contains the pure solvent. A delivery tube leads from it into a tube B graduated in c.c.'s. Towards the top of this tube there is a hole which communicates with the outer vessel C. A condenser is attached at D. A thermometer also passes into the tube B. First, a small quantity of the pure solvent is put into B, and the vapour of the solvent is blown into it until the temperature indicated by the thermometer remains constant. This temperature is noted. It is the boiling point of the pure solvent. Now a weighed amount of the substance under test is added to B, and the passage of the vapour is continued until the temperature is again constant. This is the boiling point of the solution. The volume of the solution is noted. Knowing the density of the solvent, the mass of the solvent present in the solution, assuming the solute to occupy no volume, can be found. We now have all the data necessary to enable the calculation of the molecular weight to be made.

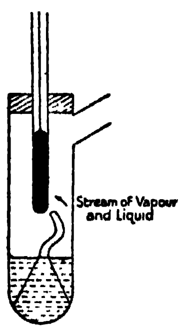


FIG. 163.—Cottrell's Apparatus.

(c) *Cottrell's Method.*—In Cottrell's apparatus an inverted funnel tube is placed in the boiling tube, which collects bubbles of vapour from a piece of porous pot in the liquid and pumps the vapour over the bulb of a thermometer, together with a stream of the boiling liquid. In this way it is ensured that the temperature indicated by the thermometer is more nearly the accurate boiling point of the liquid. The volume of solvent used is taken, and the mass of substance dissolved is known, so that the molecular weight can be calculated from a knowledge of the two boiling points. Note that in this method the bulb of the thermometer does not dip into the liquid.

(d) *Swientoslawski's Method.*—This is similar in principle to Cottrell's method in that the vapour of the liquid and a stream of boiling liquid are pumped over the thermometer bulb, but it has the advantage that the thermometer is removed from the neighbourhood of the flame, and there is little risk of superheating.

The apparatus is shown in Fig. 164, A is a bulb tube containing the solvent. A few garnets are placed at the bottom of A to prevent superheating. The wide tube C carries a Beckmann thermometer, and is provided with a metal cylinder D resting on glass points

inside the tube, to keep any direct radiation from the flame away from the thermometer. GG is an asbestos shield which serves a similar purpose. A Liebig's condenser is attached at F to return the vapour of the solvent to the boiling vessel. A known weight of solvent is placed in A, sufficient to cause a small quantity to enter the tube C. It is gently heated until it boils, when vapour and

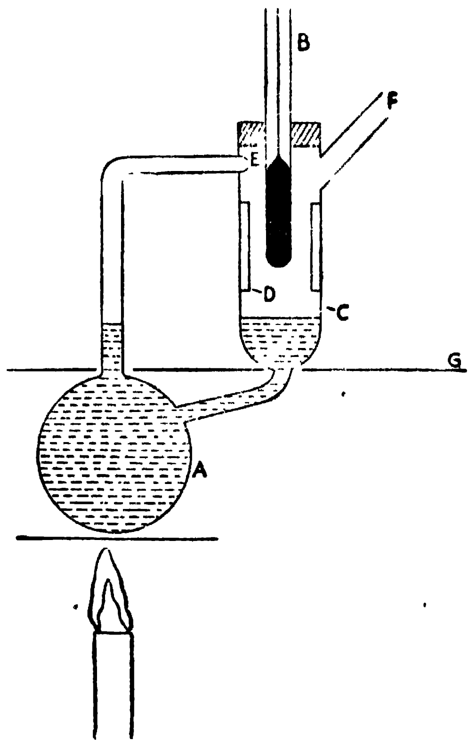


FIG. 164.—Swientoslawski's Apparatus.

liquid are pumped from the jet E over the bulb of the thermometer. The temperature indicated by the thermometer is taken when it becomes constant. A weighed pellet of the substance of which the molecular weight is required is dropped down the condenser and is dissolved by the solvent. The boiling point is again found. If desired, further weighed pellets of the solute may be added from time to time to provide further results.

As such great care is taken to avoid errors due to superheating, other errors should be minimised. Thus, the amount of solvent may decrease during the experiment if the condenser is not efficient.

This may be tested by weighing the apparatus and liquid before the experiment, and again afterwards (the condenser and thermometer may, of course, be omitted). After subtracting the weight of solute added from the latter reading, the weight of apparatus and solvent after the experiment is obtained. This should be the same as at first. If not, the amount of solvent lost may be regarded as having been lost uniformly throughout the course of the experiment, and if the time when the solute is added is known, the amount of solvent present then can be calculated. This correction is only of importance where the solvent is very volatile, *e.g.*, ether.

The rate of boiling should be kept constant by not touching the flame once the liquid has begun to boil. If the rate of boiling alters, the temperature indicated by the thermometer may be slightly altered. The least error in a molecular weight determination by elevation of the boiling point by any of the above methods, is about ± 2 per cent. This error is mainly due to the difficulty in reading the temperature. Better results can be obtained by the use of resistance thermometers, but it is doubtful whether the additional complication of the apparatus is justified. Since the method is usually employed to provide confirmation of a formula, an error of 2 per cent. in the result is usually of no account.

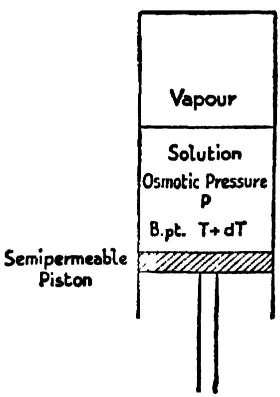


FIG. 165.—Osmotic pressure and elevation of boiling point.

239. Connection between Osmotic Pressure and Elevation of Boiling Point.—This can be obtained by considering a reversible process as follows: Suppose that we have a solution in a cylinder provided with a frictionless piston, which is semi-permeable, allowing solvent to be removed osmotically and reversibly. The osmotic pressure of the solution is P, and its boiling point $T + dT$, T being the boiling point of the solvent, and dT the elevation.

Stage I.—By moving the piston, remove a volume dv (the weight of which is dx) of the solvent at the boiling point of the solution $T + dT$. The work done is $- Pdv$.

Stage II.—Allow this volume of solvent, at temperature $T + dT$, to be evaporated isothermally. If L is the latent heat, the amount of work done is Ldx.

Stage III.—Cool the vapour and the solution to the temperature T, adiabatically (p. 195).

Stage IV.—Put the vapour in contact with the solution again at

this temperature, and allow it to condense. It gives out an amount of heat L_1dx, where L_1 is the latent heat at temperature T.

Stage V.—Raise the temperature adiabatically to $T + dT$. The amount of work in this process is equal and opposite to that in Stage III.

As the process is reversible, the algebraic sum of the work done in the various stages is equal to zero. Hence,

$$-Pdv + Ldx - L_1dx = 0,$$

or

$$Pdv = Ldx - L_1dx.$$

To find the value of the right-hand side of this expression we may apply the Second Law of Thermodynamics. Ldx is the heat taken in at temperature $T + dT$, and L_1dx is the amount of heat given up at the lower temperature T.

The Second Law (§ 315) may be put in the form

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1},$$

where Q_1 is the heat absorbed at temperature T_1, and Q_2 is that given out at temperature T_2. We thus have

$$\frac{T + dT - T}{T + dT} . Ldx = Ldx - L_1dx.$$

Hence,

$$Pdv = \frac{dT}{T + dT} . Ldx.$$

Put $dx/dv = \rho$, the density of the solvent. Then we obtain,

$$P = \frac{L\rho . dT}{T_1},$$

T_1 being the boiling point of the solution. This is the required relationship.

The solution is dilute, so the osmotic pressure obeys the law $P = cRT$. At temperature T_1 this becomes $P = cRT_1$, and hence

$$dT = \frac{RT_1^2 . c}{L . \rho},$$

which is the relationship between elevation of boiling point and concentration c.

If we take the density as being approximately unity, the equation becomes

$$dT = \frac{RT_1^2 . c}{L},$$

R is equal to 2 gm.-cals. per gram-mol. If we assume that one gram-molecule is dissolved in 100 gms. of solvent, then c becomes 0·01, and so

$$dT = \frac{2 \times T_1^2 \times 0{\cdot}01}{L} = \frac{0{\cdot}02\, T_1^2}{l} = K,$$

where K is the molecular elevation. This enables the molecular elevation to be calculated from a knowledge of the latent heat of evaporation of the solvent, and its boiling point on the absolute scale. It was first put forward as an empirical rule, but it is clear from the above that it has some theoretical basis.

The Table (p. 487) shows some values of the molecular elevation calculated for various solvents by the use of this relationship. It will be noticed that the agreement between the observed and calculated values is good.

240. Numerical Examples.—Some numerical examples will now be given in order to show exactly how data obtained from the experimental determination of the elevation of the boiling point can be used in the calculation of molecular weights.

(1) Ten gms. of a substance dissolved in 100 gms. of water raised its boiling point by 0·98° C. Calculate the molecular weight of the substance. The molecular elevation for water (100 gms.) is 5·2° C.

Since M gms. of solute (where M is its molecular weight) raise the boiling point of 100 gms. of water by 5·2° C., the weight raising it by 0·98° will be $M \times \frac{0 \cdot 98}{5 \cdot 2}$. This must be equal to 10 gms.

Hence,

$$\frac{0 \cdot 98M}{5 \cdot 2} = 10,$$

$$M = \frac{52}{0 \cdot 98},$$

$$= 53 \cdot 07.$$

The molecular weight is 53·07.

(2) What elevation of the boiling point of alcohol is to be expected when 5 gms. of urea (molecular weight 60) are dissolved in 75 gms. of it? The molecular elevation of alcohol (100 gms.) is 11·5° C.

The gram-molecular weight of urea (*i.e.*, 60 gms.) would raise the boiling point of 100 gms. of alcohol by 11·5° C. Five gms. of urea would therefore elevate the boiling point of 100 gms. of alcohol by $\frac{11 \cdot 5}{12}$ °C.

As the urea is dissolved in 75 gms. alcohol, the elevation will be

$$\frac{11 \cdot 5 \times 100}{12 \times 75} \text{°C.} = 1 \cdot 28\text{° C.}$$

241. Limitations of the Method.—In addition to the occurrence of abnormalities in the molecular weights of substances determined by this and all colligative property methods, which are to be noted later on (§ 246), it must be borne in mind that the solutes that can be used in the boiling-point method are limited to those which are

not volatile. The substance dissolved must remain entirely in the liquid phase during the experiment. The method could not, then, be used to find the molecular weight of a substance like alcohol, or any other easily volatile substance. It has been pointed out by Lowry that the escape of the solute into the vapour phase corresponds to having a leaky membrane in determination of osmotic pressure.

242. Depression of the Freezing Point.—Just as lowering of the vapour pressure causes directly an elevation of the boiling point, so it directly conditions a depression of the freezing point. That this must be so follows from a consideration of the vapour pressure curves of the solid solvent, the liquid solvent, and the solution. These are shown in Fig. 166. The freezing point of the pure solvent

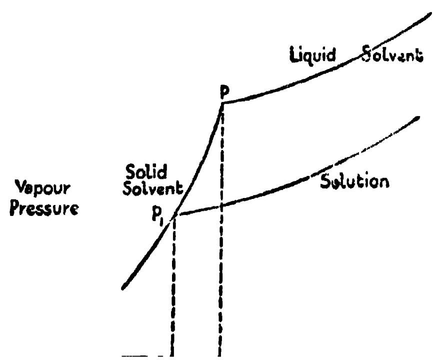


FIG. 166.

is given by the abscissa of the point P, where the vapour pressure curves of the solid and liquid solvent intersect. If the vapour pressure of the solution is less than that of the liquid solvent, the vapour pressure curve of the solution must intersect the curve for the solid solvent at a point P_1, corresponding to a lower temperature. Equimolecular weights of substances dissolved in the same weight of a solvent depress its freezing point by the same amount.

The first experiments on the depression of the freezing point were carried out by Blagden in 1788. He noticed that the freezing point of water was depressed by the presence of dissolved salts, and that the depression was proportional to the concentration. His results were, however, overlooked, until revived by de Coppet in 1871, and by Raoult in 1882–84.

As in the case of the elevation of the boiling point, a table can be drawn up giving the molecular depression for certain solvents. The

figures given (Table LXXXI) are those obtained by the solution of one gram-molecule in 100 gms. of the solvent. Note that the figures are not the same as for the elevation of the boiling point.

243. Experimental Determination of the Depression of the Freezing Point.—The best method is that due to Beckmann. The apparatus is shown in Fig. 167. It consists of a large outer vessel, which contains a freezing mixture. A tube, about the size of a large boiling tube, is suspended in this, and inside that is the freezing tube, which is provided with a side tube for the introduction of the weighed solid, a stirrer, and a Beckmann thermometer. The thermometer is first set so as to obtain the freezing point of the pure solvent towards the top of the scale. The apparatus is then set up and the freezing point of a known weight of the solvent is determined. The solvent is allowed to supercool a little below its freezing point, and is then stirred vigorously in order to start crystallisation. As the freezing starts the temperature rises, and remains steady at the freezing point. A weighed pellet of the substance under investigation is now added through the side tube, completely dissolved, and the freezing point of the solution found. Any considerable degree of supercooling should be avoided, since separation of much solid solvent increases the concentration of the solute.

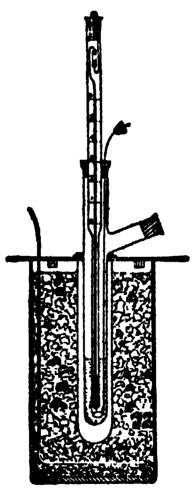


FIG. 167. — Beckmann's Freezing-point Apparatus.

Rast's method makes use of the fact that camphor has a very high molecular depression. One gram-molecule of a substance dissolved in 1,000 gms. of camphor produces a depression of 40° C. In this case the depression is so great that an ordinary thermometer may be used for the determination of the freezing point.

A known weight of the substance under investigation is mixed with a known weight of camphor, and the two are intimately fused together, the mass allowed to cool and then broken up. The melting point of the mixture is then determined in the usual way in a capillary tube. The melting point of pure camphor is also determined. The molecular weight is then calculated from a formula similar to that for elevation of boiling point (p. 488).

Some compounds with higher depression constants than camphor are known. They are all members of the hydroaromatic class. Pirsch (1933) has found that camphorquinone has a high constant (457° C. for 100 gms.), and has a fairly high melting point (197·2° C.),

TABLE LXXXI.—MOLECULAR DEPRESSION
(per 100 gms. solvent)

Solvent.	$K°$ C.	K calc. $\frac{0{\cdot}02T^2}{L}$.
Water	18·5°	18·6°
Acetic acid	39°	38·2°
Phenol	53°	50·5°
Camphor	400°	—
Naphthalene	69°	69·5°
Benzene	51·2°	50·7°
Camphor quinone	457°	—
Pinene dichloride	562°	—
Pinene dibromide	809°	—
Bornylamine	406°	—

and high solvent properties. With pinene dichloride and pinene dibromide, the constants are 562° C. and 809° C. respectively. These two substances form a continuous mixed crystal system, and the depression constant is additive for these mixtures, *i.e.*, it is a function of the composition of the mixture. Bornylamine gives a molecular depression constant of 406° C., and is especially useful in determining the molecular weights of alkaloids. It has the disadvantage of being very volatile at the melting point, and hence sealed melting point tubes must be used.

Raoult suggested that there might be some connection between the molecular depression and the molecular weight of the solvent, but no simple relationship has been discovered.

244. Connection between Osmotic Pressure and Depression of the Freezing Point.—By means of a thermodynamic cycle exactly similar to that used in the case of elevation of boiling point, the relationship between osmotic pressure and depression of the freezing point can be derived. The student is recommended to attempt this for himself.

The final relationship is

$$P = \frac{L\rho \, . \, dT}{T_s},$$

where ρ is the density of the solvent, dT, the depression of the freezing point, and T_s the freezing point of the solution, and L the latent heat of fusion of the solvent. As before, we can substitute the value of the osmotic pressure and obtain the expression

$$dT = \frac{RT_s^2 \, . \, c}{r}.$$

This gives, as before,

$$K = \frac{0{\cdot}02T^2}{L}.$$

This enables the molecular depression, K, to be calculated if the latent heat of fusion of the substance, L, and its freezing point on the absolute scale are known.

245. Numerical Examples.—(1) Fifteen gms. of a substance dissolved in 150 gms. of water lowered its freezing point by 1·2° C. Find the molecular weight of the substance. The molecular depression for water is 18·5° C. (100 gms.).

Since 15 gms. of substance are dissolved in 150 gms. of water, 10 gms. are dissolved in 100 gms. of water.

One gram-molecule of the substance, dissolved in 100 gms. of water, depresses the freezing point by 18·5° C. Hence, if M is the molecular weight of the substance, $\frac{M \times 1{\cdot}2}{18{\cdot}5}$ gms. of it will depress the freezing point of water by 1·2° C. This weight must be equal to 10 gms.

$$\therefore \frac{1{\cdot}2M}{18{\cdot}5} = 10$$

$$M = \frac{185}{1{\cdot}2}$$

$$= 154{\cdot}2.$$

(2) A sample of pure prismatic sulphur melted initially at 119·25° C., but in the course of a few minutes the melting point fell to 114·5° C. When the sulphur had completely melted at this temperature the liquid sulphur was plunged into iced water; 3·6 per cent. of the resultant solid sulphur was then found to be insoluble in carbon disulphide. Deduce the molecular formula of the type of sulphur insoluble in carbon disulphide. The latent heat of fusion of sulphur is 9 cals. per gram. (St. Catharine's College, Cambridge, Schol., 1932.)[1]

We can obtain the molecular depression of sulphur, K, from the Rule (§ 244),

$$K = \frac{0{\cdot}02T^2}{L},$$

where T is the freezing point of the pure sulphur on the absolute scale and

L is the latent heat of fusion.

Now, $T = 119{\cdot}25°$ C. $= 392{\cdot}25°$ Abs.

[1] This question is quoted by permission of the Syndics of the Cambridge University Press.

and $L = 9$ cals. per gram.

$$\therefore K = \frac{0{\cdot}02 \times (392{\cdot}25)^2}{9}$$
$$= 341{\cdot}8^\circ \text{ C.}$$

After the melting, some Sλ is formed, and the melting point is lowered. 100 gms. of the mixture contain 3·6 gms. of Sλ. Hence, 96·4 gms. of solvent contain 3·6 gms. of solute. The depression is $119{\cdot}25^\circ - 114{\cdot}5^\circ = 4{\cdot}75^\circ$. Let M be the required molecular weight. Then, M gms. dissolved in 100 gms. of sulphur depress the freezing point by 341·8° C.

Hence, $\frac{M}{341{\cdot}8} \times 4{\cdot}75$ gms. in 100 gms. of sulphur depress the freezing point by 4·75° C., and $\frac{M}{341{\cdot}8} \times \frac{4{\cdot}75 \times 100}{96{\cdot}4}$ gms. in 96·4 gms. of sulphur depress the freezing point by 4·75° C.

This weight must be equal to 3·6 gms.

$$\therefore M = \frac{3{\cdot}6 \times 341{\cdot}8 \times 96{\cdot}4}{4{\cdot}75 \times 100}$$
$$= 249{\cdot}8.$$

This corresponds to the formula S_8 (approximately).

246. Abnormal Molecular Weights.—It is clear that since all the properties described in this chapter are proportional not to the weight of substance dissolved, but to the molecular concentration of the solution, the effects must be due to the numbers of molecules of solute in the solution. If, then, a substance does not dissolve as single molecules, the effects will not indicate the true molecular weight of the substance as shown by the formula.

Thus, if a substance associates in the solvent, then the number of individual particles present will be half what there would be if association did not occur (assuming the association of single into double molecules). The molecular weight indicated by these methods will then be double the true molecular weight, as indicated by the formula.

Similarly, if dissociation occurs (§ 251), as it does whenever a metallic salt is dissolved in water, the number of individual particles (this time the ions) is greater than the number of molecules that there would otherwise be in the solution, and the molecular weight indicated by these methods is smaller than that derived from the formula of the substance.

Van't Hoff introduced into the osmotic pressure equation a factor i, which would include these anomalies. The osmotic pressure equation then becomes

$$PV = iRT.$$

For normal solutions $i = 1$, but for abnormal solutions the factor is obtained by dividing the experimental value for the molecular depression by the normal value. Thus, when one gram-molecule of sodium chloride is dissolved in 100 gms. of water the molecular depression is 36, whereas the value for a normal substance is 18·5. Hence, $i = 36/18{\cdot}5 = 1{\cdot}94$.

It is possible to calculate the degree of association or dissociation from the values of the molecular weight determined by any of these methods. Let us consider first the case of *association*. Let the degree of association be x, and n the number of molecules which come together to make the associated molecule. The amount of simple molecules left will be $1 - x$. The amount of associated molecules formed will be x/n. Hence, the number of particles in solution will have been reduced by the ratio $1/(1 - x + x/n)$. If the molecular weight is determined by the depression of the freezing point and F_o is the observed depression, and F_c the calculated depression assuming no association, then

$$\frac{F_o}{F_c} = \frac{1 - x + \frac{x}{n}}{1}.$$

$$x = \frac{F_c - F_o}{F_c\left(1 - \frac{1}{n}\right)},$$

but $\quad \dfrac{M_c}{M_o} = \dfrac{F_o}{F_c}$, where M_c = calc. molecular weight, M_o = observed molecular weight

$$\therefore x = \frac{M_o - M_c}{M_o\left(1 - \frac{1}{n}\right)}.$$

For dissociation, let x be the degree of dissociation and n the number of ions formed from one molecule, then the actual number of particles present is $1 - x + nx$ times greater than it would be in absence of dissociation, and the ratio F_o to F_c is given by

$$\frac{F_o}{F_c} = \frac{1 - x + nx}{1},$$

$$\therefore x = \frac{M_c - M_o}{M_o(n - 1)}.$$

SUMMARY

The laws of dilute solutions derived in this chapter hold only for ideal solutions. An ideal solution is one for which the volume change accompanying a small dilution is additive.

When two solutions of the same substance are added to each other carefully to avoid mixing, two separate layers are formed, but after some months, even if convection currents are prevented, the solutions are found to be completely mixed. The force which causes the equal distribution of the molecules is the osmotic pressure. If two solutions of different concentration are separated by a membrane which is permeable to water, but not to the solute molecules (a semi-permeable membrane), water will pass through the membrane from the weaker solution into the stronger one, and, if pure water is placed on one side of the membrane, the hydraulic pressure set up is the osmotic pressure of the solution. Solutions having the same osmotic pressure are called "isotonic solutions." The osmotic pressure of a solution is proportional to the concentration, and proportional to the absolute temperature. The equation governing osmotic pressure is, therefore, $PV = KT$, where P is the pressure, V the volume of solution containing 1 gram-molecule of solute, T the absolute temperature, and K a constant. When K is calculated it is found to be identical with the gas-constant R (Chapter V.). Thus, the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature, and occupying the same volume as the solution. Observation of the osmotic pressure of a solution enables the molecular weight of the solute to be calculated, but the practical determination is difficult. There is no satisfactory theory of semi-permeability or osmotic pressure. The laws governing gaseous and osmotic pressure, shown to be identical by experiment, can be proved to be so by thermodynamics.

Raoult's Law of Vapour Pressure Lowering states that the vapour pressure of a solution is proportional to the mol-fraction of the solvent present in the solution. Mathematically,

$$\frac{p_o - p_s}{p_o} = \frac{n}{N + n},$$

where p_o and p_s are the vapour pressures of the solvent and the solution respectively, n is the number of molecules of solute, and N is the number of molecules of solvent in the solution. Observations of lowering of vapour pressure can be used for determining molecular weights of solutes. The methods of determining the lowering are (*a*) static, in which the pressure is directly measured in a barometer tube; and (*b*) dynamic, *e.g.*, the method of Walker and Ostwald. The dew-point method can also be used.

Since solutions have a smaller vapour pressure than that of the pure solvent, they must also have a higher boiling point and a lower freezing point. Equimolecular weights of different substances will raise the boiling point of a solvent by the same amount, or lower its freezing point by the same amount. This relationship may be used for determining molecular weights of substances in solution, if the elevation of the boiling point or depression of the freezing point caused by dissolving one gram-molecule of a substance in a known weight of solvent (100 gms. is usually taken) is known. The methods of determining molecular weights of substances in solution, depending upon colligative properties, are applicable mainly to non-electrolytes, such as organic substances. Abnormal molecular weights are shown by substances which are either associated, or dissociated (electrolytes), in solution.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 30.—Determine the molecular weight of urea by the vapour pressure method.

Fit up the apparatus as described on p. 484. The dynamical method is to be used. Aspirate air through the apparatus for about six hours.

Experiment 31.—Determine the molecular weight of urea in water by the freezing point method.

Use the method described on p. 496. Rast's method should also be tried, using naphthalene in camphor.

Also show that potassium chloride in water gives anomalous results.

Experiment 32.—Determine the molecular weight of cane-sugar in water using the Landsberger method.

Details for all these experiments will be found in the text, and the student is advised also to try several others which will be found in the text-books of Practical Physical Chemistry, such as that by Sherwood Taylor, or by Findlay.

SUGGESTION FOR FURTHER READING

FINDLAY, A. "Osmotic Pressure." (*Longmans.*)

QUESTIONS

(1) Describe a method of finding the molecular weight of a substance in solution.

When 0·25 gm. of a substance was dissolved in 100 gms. of water, the freezing point of the latter was lowered by 0·43° C. Find the molecular weight of the substance (molecular depression for water = 18·5° C.).

(2) What methods are available for the determination of the molecular weight of (*a*) a gas, (*b*) a non-volatile electrolyte ? Describe in detail one method for the latter class.

(3) Write an essay on the properties of dilute solutions.

(4) Show how the osmotic pressure of a solution is connected with the elevation of the boiling point.

(5) The boiling point of acetone is 56·38° C. A solution of 0·564 gm. of a compound in 8·6 gms. of acetone boiled at 56·75° C. What was the molecular weight of the compound ? (Molecular elevation for acetone = 16·7° C.)

(6) How may observations of the vapour pressure of a solution be used to give information concerning the molecular weight of the substance dissolved ?

(7) How is the latent heat of evaporation and of fusion of a substance connected with the molecular elevation or depression respectively ?

(8) The following results were obtained by Morse in experiments on the osmotic pressure of mannitol ($C_6H_{14}O_6$) :—

Grams Mannitol in 100 gms. Water.	Osmotic Pressure, 10° C.	Osmotic Pressure, 40° C.
1·82	2·314 atm.	2·557 atm.
3·64	4·609 „	5·107 „
5·46	6·940 „	7·664 „
7·28	9·209 „	10·216 „

Show that these data agree with the Laws of Osmotic Pressure.

(9) Raoult found that a solution of 11·346 gms. of turpentine in 100 gms. of ether, $(C_2H_5)_2O$, had a vapour pressure of 360·1 mm. At the temperature of the experiment, the vapour pressure of pure ether was 383 mm. Calculate the molecular weight of turpentine.

(10) Will and Bredig (1889), using the dynamic method of determining the vapour pressure lowering of alcoholic solutions, found the following results :—

Substance.	Weight dissolved in 30 gms. alcohol. Gms.	b_1. Gms.	b_2. Gms.
Nitrobenzene .	4·1	2·034	0·0684
Benzoic acid .	4·28	1·8315	0·0731
Acetamide . .	5·04	0·6073	0·0525
Atropine . .	5·05	1·467	0·027
Vanillin . .	2·4	1·6895	0·0312

b_1 is the loss in weight of the set of bulbs containing the solution, and b_2 is the loss in weight of the bulbs containing alcohol. Calculate the molecular weights of these substances from the above data.

(11) Beckmann (1890) found the molecular weight of iodine as follows : 1·065 gms. of iodine were dissolved in 30·14 gms. of ether. The boiling point of the ether was raised by 0·296° C. The molecular weight of ether is 74, and the molecular elevation constant 21·1° C. Calculate the molecular weight of iodine.

(12) Andrews found the heat of vaporisation of 1 gm. of carbon disulphide to be 86·72 cals. Its boiling point is 46° C. Calculate the molecular elevation constant.

Beckmann found that 1·4475 gms. of white phosphorus dissolved in 54·65 gms. carbon disulphide raised the boiling point by 0·486° C. Calculate the molecular weight of white phosphorus.

(13) Pirsch found that 0·685 milligrams of anthraquinone dissolved in 8·943 milligrams of camphorquinone lowered the melting point of the latter by 16·6° C. If the molecular depression for camphorquinone is 457° C., calculate the molecular weight of anthraquinone.

(14) 0·806 milligrams of naphthalene $(C_{10}H_8)$, when dissolved in 9·930 milligrams of bornylamine, produced a depression of the freezing point of 32·5° C. Calculate the molecular depression for bornylamine.

(15) In determining the molecular weights of the alkaloids caffeine and morphine, Pirsch obtained the following results :—

Solvent—Bornylamine. $K = 406°$ C.

	Wt. of Solute. Mgms.	Wt. of Solvent Mgms.	Depression of Freezing Point. ° C.
Caffeine . .	0·568	7·132	16·1
Morphine . .	0·876	10·624	11·6

Calculate the molecular weights of these substances. The theoretical values are : caffeine 212, morphine 303.

(16) H. J. S. King, in research on ammines, found the apparent molecular weight of diamminocupric acetate by the boiling point method. 0·3998 gm. of the salt was dissolved in 21·05 gms. of anhydrous alcohol. The boiling point was raised by 0·035° C. The molecular elevation for alcohol is 11·5° C. Calculate the apparent molecular weight of the salt.

(17) The molecular weight of selenium oxychloride, $SeOCl_2$, in dry benzene, was determined by Henley and Sugden (*J. C. S.*, 1929, 1064), using the freezing point method. The following results were obtained:—

Concn. (gms. per 100 gms. of Benzene).	Depression, ° C.
1·925	0·578°
4·713	1·345°
6·06	1·641°

Calculate the molecular weight of selenium oxychloride from each of these observations. To what conclusion do they lead concerning the molecular condition of selenium oxychloride in benzene solution ?

CHAPTER XII

ELECTRICAL CONDUCTION IN SOLUTIONS AND METALS

247. Types of Conductor.—Fairly early in the history of electricity it was realised that solid substances fell roughly into two classes—conductors of electricity and non-conductors, or insulators. This was known before the discovery of the phenomena of voltaic electricity. When, however, Volta made his cell (1799), the conduction of electricity by liquids was investigated, and in the year after the cell was made (1800) the products of decomposition of water when the current was passed through it were being studied. It was soon discovered that most liquids, unlike solids, were decomposed by the current when it was passed through them. As soon as the current stopped, the decomposition ceased, indicating quite clearly that the decomposition was in some way bound up with the passage of the current. Also, the products appeared only at the poles, where the electricity entered or left the solution. The decomposition was not general. These liquids, which undergo decomposition, were later called *electrolytes* by Faraday. He also gave names to the poles, the positive pole, at which the electricity was supposed to enter the solution, being called the *anode*, and the negative pole, where it was supposed to leave, the *cathode*.

Since that time it has been discovered that it is solutions of acids, bases and salts which undergo decomposition in this way.

All that is apparent in electrolysis is a decomposition of the solution at the electrodes. It may be pointed out that a certain minimum electromotive force must be applied to the electrodes before electrolysis will occur. This minimum voltage varies from electrolyte to electrolyte, and also depends upon the nature of the electrodes. The reason for its existence is that the products of the electrolysis in contact with the electrodes cause a back electromotive force (e.m.f.), which must be overcome before electrolysis will take place. It is called a polarisation e.m.f. The hydrogen gas in contact with the platinum electrode in the electrolysis of water causes a back e.m.f., since it acts as a voltaic cell. Where there is no polarisation, this minimum e.m.f. is no longer necessary. Thus, the smallest applied potential will carry out the electrolysis of copper sulphate between copper electrodes. In all cases there is a small

amount of decomposition as soon as the e.m.f. is applied, no matter how small it is, but unless the applied e.m.f. is greater than the polarisation e.m.f. there is no further decomposition (see also § 325).

248. The Grotthus Chain Theory.—The peculiar fact that decomposition in electrolysis takes place only at the electrodes and not in the bulk of the solution was first explained by Grotthus in 1805. He supposed that the passage of the current, and the chemical changes produced by it, were due to the successive decomposition and recombination of particles of the dissolved substance. In Fig. 168 the molecules are AB, AB, etc. As soon as the electrodes are placed in the solution, these molecules are turned in the direction shown in the figure (I). Owing to the attraction of the electrodes, A is split off at one end, and the B part of the molecule finds itself free (II), so it attacks the next molecule to it, depriving it of its A portion. This goes on all along the chain until the B part of the end molecule next the electrode finds itself without any further molecules to

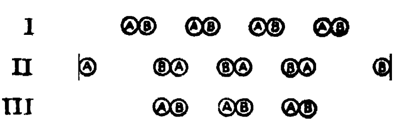


FIG. 168.—The Grotthus Chain Theory.

attack, and so is liberated at the electrode opposite to that at which the A was originally set free. It will be seen from this theory that the two parts of the molecule liberated in electrolysis do not come from the same molecule, but from entirely different ones. When the B part has been liberated it is seen from the figure that the molecules are all the reverse way round to what they were to start with, and so, before further decomposition takes place, they must all be turned round by the attractive force of the electrodes (III).

This theory was disproved by the fact that Ohm's Law (which states that the current (I) flowing in a circuit is proportional to the applied electromotive force (E), the ratio E/I being the resistance R) was found to apply to solutions of electrolytes, and hence all the electrical energy was used in overcoming the resistance of the solution and none in breaking up the substance into the parts A and B referred to above.

249. Faraday's Laws of Electrolysis.—The quantitative laws governing the decomposition of electrolytes by the electric current were derived by Faraday in 1834. These have been referred to already in Chapter II. (p. 52), but will be repeated here. Faraday

gave the name "ions" to the parts into which the molecule was decomposed on solution (§ 251). His two Laws of Electrolysis are :—

(1) The amount of decomposition caused in electrolysis is proportional to the quantity of current passed.

(2) For the same quantity of electricity passed through different solutions the amount of decomposition is proportional to the equivalent of the element, or group, liberated.

Thus, if the same current is passed for the same time through solutions of copper sulphate, silver nitrate, lead nitrate, ferrous sulphate, and ferric sulphate, the amounts of metal deposited at the cathode are proportional to the equivalents of the metals, *i.e.*, to 31·78, 53·94, 103·61, 27·92, 18·61 respectively.

The verification of these Laws is a fairly simple matter, and is dealt with in Physics.

250. The Theory of Clausius.—After the failure of the Grotthus chain theory to account satisfactorily for all the facts of electrolysis, no further theory seems to have been put forward until that of Clausius in 1857. It is true that Faraday modified the Grotthus theory, but not to any great extent. Clausius stated that in solution an electrolyte is invariably split into its ions, and that there is an equilibrium between the ions and the undissociated electrolyte. Only a minute proportion of the free ions was supposed to exist at any one time. The free ions were charged, and therefore travelled towards the electrodes bearing the opposite charges, and there became discharged and liberated as the ordinary products of electrolysis.

This theory was satisfactory, but there was no quantitative expression bound up with it. That was left to Arrhenius.

251. The Arrhenius Theory of Electrolytic Dissociation.—It has been mentioned (§ 246) that metallic salts give anomalous results in osmotic pressure determinations, and that van't Hoff therefore introduced the factor i in the expression

$$PV = iRT$$

to cover these anomalies. Similar anomalies were also found in the lowering of the vapour pressure, and depression of freezing point, and elevation of the boiling point, since all these properties are connected with osmotic pressure. Arrhenius (1887) stated that these anomalies could be accounted for if it were assumed that the dissolved substance were partly broken up into electrically charged atoms or groups, called ions, and this assumption was supported by the fact that the substances which gave the anomalous results were all of them electrolytes. Arrhenius took this view not only on the basis of abnormalities in osmotic pressure and other

colligative properties, but also as a result of a great deal of work on the conductivity of solutions of electrolytes. On the basis of the results of osmotic pressure and electrical conductivity he was able to state the extent of the ionisation.

This view was also put forward by Planck in the same year, though he studied it from the point of view of thermodynamics. He was able to say that the observed abnormalities of freezing point, etc., could only be brought into harmony with thermodynamical laws if the molecules were supposed to be broken down into parts to some extent.

This theory of electrolytic dissociation has played a very great part in the development of electrochemistry. According to this theory we must suppose that immediately a metallic salt is dissolved in water it is at least partly dissociated into its ions, which are free and moving about with random motion in the liquid. When the e.m.f. is applied, the ions are attracted towards the electrodes bearing the opposite sign, and when they reach it they are discharged and appear at the electrode in their normal condition.

This theory, when it was first put forward, met with the greatest opposition, and some of the arguments against it are worth while mentioning here. The arguments for it are given later (§ 267).

(1) In many cases the ions produced were of substances which would react with water in the ordinary state. It was argued that the sodium ion could surely not exist in the presence of water, having regard to the well-known violent action of sodium on water. Also chlorine could surely not exist in the free state in a solution of sodium chloride, since it is a green gas. But this argument arises from a misconception of the theory. The theory states that the ions of these substances, and not the substances themselves, exist in solution. The ions are the charged atoms or groups, having lost or gained electrons (§ 59). The point is very clearly brought out when we consider the difference between an ion and an atom according to the electronic theory.

(2) It was said that the affinity between the different parts of the molecule, *e.g.*, sodium and chlorine in sodium chloride, was very great, and that the mere fact of solution in water should be insufficient to break down the bond between them. It is not, however, the affinity between the atoms, but that between the ions, that is in question. It is now known that common salt is ionised even in the solid state.

(3) If there are ions in solution it was argued that it ought to be possible to separate them by diffusion. The electrical charges carried by the ions would however tend to prevent this; being equal and opposite, they would tend to keep the ions in the form in

which they occur in the space lattice of the crystal. It is, however, possible to effect a slight separation by diffusion. Tolman (1911) centrifuged solutions of certain iodides, and found that the ends of the tubes containing the solution became charged oppositely, presumably owing to the heavier iodide ions being in excess at one end, and the lighter metal ions at the other.

(4) It was at first thought that all instantaneous reactions in solution were due to interaction between ions. Several such reactions between substances in non-conducting solutions were, however, discovered, and these were brought forward as arguments against the dissociation theory. It is now known that instantaneous reaction need not necessarily take place between ions, so this argument carries no weight.

Numerous other objections were put forward, and other methods of explaining the anomalies in the colligative properties were given, but all have been shown to be of no importance. The evidence for the truth of the theory of dissociation is now so strong that it is held by every chemist.

The view of Arrhenius was that *all* electrolytes are *partly* dissociated into their ions on solution in water. It is now believed that certain substances, called *strong electrolytes* [1] (*e.g.*, sodium chloride, hydrochloric acid, etc.), are completely dissociated in aqueous solution. The apparent degree of dissociation shown by these electrolytes is due to interionic forces. This view will be developed in greater detail in Chapter XIII.

252. Electrolysis.—For purposes of revision, a few examples of electrolysis are given here. The outline schemes are self-explanatory.

(1) *Electrolysis of Dilute Sulphuric Acid.*—The solution contains hydrogen and sulphate ions (and also HSO_4^- ions). The first are charged positively, the rest negatively. The total charges on the ions must be equivalent, as the solution is not charged. When two electrodes connected to the poles of a battery are placed in the solution, the positively charged hydrogen ions travel to the cathode. There they gain electrons from the negatively charged plate, and become neutralised, and are liberated as ordinary hydrogen. The sulphate ions are attracted to the anode, where they give up their electrons and are neutralised. The sulphate radical, however, reacts immediately with water, and instead of being set free as the radical, it re-forms sulphuric acid, and oxygen is given off. The net

[1] Strong electrolytes are those electrolytes which do not obey Ostwald's Dilution Law (§ 271), and the class comprises most electrolytes which give good conducting solutions at moderate dilutions. This definition will be more clearly understood after reading Chapter XIII.

effect is the formation of hydrogen and oxygen at the electrodes (actually it is just as if water itself had been electrolysed). The reaction between the sulphate radical and water is known as a "secondary" effect. The occurrence of these secondary effects frequently makes the results of electrolysis very complicated. The electrolysis of dilute sulphuric acid between platinum electrodes may be represented by the following scheme :—

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$

$$\swarrow \text{cathode} \qquad \searrow \text{anode}$$

$$\begin{array}{ll} 2H^+ + 2\epsilon = 2H & SO_4^{--} - 2\epsilon = SO_4 \\ 2H = H_2 & 2H_2O + 2SO_4 = 2H_2SO_4 + O_2. \end{array}$$

If the acid is about 50 per cent., there is a large proportion of HSO_4^- ions, and if a point anode is used (to give high current density) the conditions are favourable for the production of persulphuric acid, $H_2S_2O_8$.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$\swarrow \text{cathode} \qquad \searrow \text{anode}$$

$$\begin{array}{ll} H^+ + \epsilon = H & HSO_4^- - \epsilon = HSO_4 \\ 2H = H_2 & 2HSO_4 = H_2S_2O_8. \end{array}$$

(2) *Electrolysis of Sodium Hydroxide Solution between Platinum Electrodes.*

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$\swarrow \text{cathode} \qquad \searrow \text{anode}$$

$$\begin{array}{ll} Na^+ + \epsilon = Na & OH^- - \epsilon = OH \\ 2Na + 2H_2O = 2NaOH + H_2 & 4OH = 2H_2O + O_2. \end{array}$$

(3) *Electrolysis of Copper Sulphate Solution between Platinum Electrodes.*

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\swarrow \text{cathode} \qquad \searrow \text{anode}$$

$$\begin{array}{ll} Cu^{++} + 2\epsilon = Cu & SO_4^{--} - 2\epsilon = SO_4 \\ & 2SO_4 + 2H_2O = 2H_2SO_4 + O_2. \end{array}$$

(4) *Electrolysis of Copper Sulphate Solution between Copper Electrodes.*

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\swarrow \text{cathode} \qquad \searrow \text{anode}$$

$$\begin{array}{ll} Cu^{++} + 2\epsilon = Cu & SO_4^{--} - 2\epsilon = SO_4 \\ & Cu + SO_4 = CuSO_4. \end{array}$$

The anode dissolves, and copper is deposited on the cathode. The

chief effects of electrolysis are summed up in the following Table :—

TABLE LXXXII.—EFFECTS OF ELECTROLYSIS OF AQUEOUS SOLUTIONS OF VARIOUS SUBSTANCES

Substance Electrolysed.	Cathode.	Anode.
(1) Acid	Hydrogen, or product of reaction of the acid with nascent hydrogen.	Product of reaction of the acid radical :— (*a*) With itself, *e.g.*, $Cl + Cl = Cl_2$; $CN + CN = (CN)_2$. (*b*) With the anode, if of reactive material, *e.g.*, $Cu + SO_4 = CuSO_4$. (*c*) With water, the acid being re-formed, and oxygen evolved, *e.g.*, $SO_4 + H_2O = H_2SO_4 + O$. (*d*) Breakdown of the acid radical, *e.g.*, $2CH_3COO' = C_2H_6 + 2CO_2$.
(2) Salt of fairly electropositive metal (*e.g.*, Na, K, Ca).	Hydrogen and hydroxide, or oxide of metal.	As above, with the addition of (*e*) product of interaction of the acid radical with the cathode liquid, *e.g.*, $2NaOH + Cl_2 = NaOCl + NaCl + H_2O$.
(3) Salt of "heavy" or noble metal.	Metal.	As above.
(4) Salt of ammonium or amine.	Hydrogen and free ammonia, or amine, or amine hydroxide, if stable.	As above.

253. The Determination of the Conductivity of an Electrolyte.— The resistance of a circuit is given by Ohm's Law as the ratio of the applied voltage to the current which flows. Thus

$$E/I = R,$$

where E is the voltage in volts, I the current in ampères, and R the resistance in ohms.

In order to be able to compare the resistances of different substances, the *specific resistance* is used. This is defined as *the resistance of a specimen of the material of length* 1 *cm., and* 1 *sq. cm. area of cross-section.* The specific resistance is sometimes called the *resistivity.* If l is the length of a conductor, and a its area of cross-section, and R its resistance, then it follows that

$$R = Sl/a,$$

where S is the specific resistance.

The *reciprocal of the specific resistance* is called the *conductivity*, κ, or sometimes the *specific conductance* of the material.

These definitions apply equally to electrolytes and to solids, though the matter is somewhat complicated in the case of electrolytes by the conductivity being dependent upon concentration, and therefore, to obtain comparable results for different solutions, it is necessary to compare their conductivities at equivalent concentrations.

The *equivalent conductivity* is defined as the *specific conductance multiplied by the volume in c.c. containing* 1 *gm. equivalent of the electrolyte.* It is usually given the symbol Λ. Hence if κ is the specific conductivity, and V the volume containing 1 gm. equivalent,

$$\Lambda = \kappa V.$$

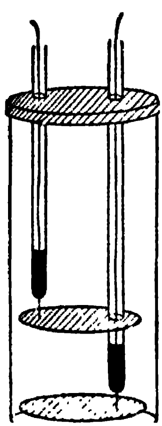


FIG. 169.—Conductivity Cell.

The *molecular conductivity* is the *specific conductance multiplied by the volume in c.c. containing one gram-molecule of the electrolyte.* It is usually given the symbol μ.

Having defined the terms, it is now possible to proceed to the method of determining the conductivity of an electrolyte. We will suppose that we require the equivalent conductivity of a solution of common salt at 15° C. The temperature must be specified, since the resistance varies considerably with temperature.

A modification of the Wheatstone's bridge method of determining the resistance of a solid conductor is used. The solution of which the resistance is required is placed in a special cell, a common form of which is shown in Fig. 169. It is necessary that the distance between the electrodes should remain quite fixed during an experiment, yet it is desirable not to have them permanently fixed. The distance apart of the electrodes and their area of cross-section must be known, if it is desired to determine the conductivity of a substance without the use of a reference electrolyte. It is very difficult to measure these, and so it is usual to determine the resistance of a solution of potassium chloride of known concentration $\left(\text{usually } \frac{N}{10}\right)$ in the cell, and, from the known conductivity of this solution, to calculate the "cell constant," *i.e.*, the factor by which the observed resistance has to be multiplied to obtain the specific resistance of the electrolyte.

When a current is passed through an electrolyte, polarisation of

the electrodes occurs if gases are evolved during the electrolysis. The presence of the layer of gas at the electrodes causes a considerable increase in the resistance, and in conductivity measurements must be prevented. This is usually done by employing a rapidly alternating e.m.f., which, if it is symmetrical, produces no polarisation, the polarisation produced by one half of the wave being immediately neutralised by that due to the other half. As a source of the alternating current, Kohlrausch used a small induction coil, though actually this gives not pure alternating current, but a pulsating direct current, and cannot be used for very accurate work. High-frequency generators have been used, but recently the ordinary wireless valve has been employed. It is found that the conductivity of a solution varies with the frequency of the current used, so that for very accurate work the frequency should be known. Further,

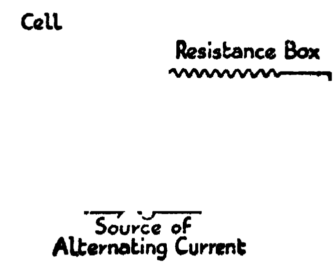


FIG. 170.—Circuit for determining Conductivity.

to avoid polarisation, the electrodes, which are of platinum, are coated with platinum black by electrolysing a solution of platinum chloride in the cell before any experiments are done with it.

An ordinary galvanometer will not detect an alternating current. Galvanometers can be made for alternating current, but they are not, as a rule, so sensitive as direct-current instruments. Telephones are frequently used, sometimes in conjunction with a valve amplifier, for greater sensitivity.

The circuit is arranged as shown in Fig. 170. The sliding contact C is moved along the bridge wire AB, until the position of minimum sound in the telephones T is obtained. The ratio of the lengths of the bridge wire is equal to the ratio of the resistances :—

$$\frac{\text{Resistance of electrolyte}}{\text{Resistance in box}} = \frac{AC}{BC}.$$

In carrying out an experiment, the electrodes of the cell are first platinised by putting some platinum chloride solution into the cell, and passing the current for half-minute intervals in each direction. When the electrodes are thoroughly blackened, they are removed, and the cell and electrodes thoroughly washed with distilled water.

The cell is now filled with distilled water, and its resistance determined. If the resistance is less than $2-4 \times 10^6$ ohms, the electrodes still contain soluble matter, which must be removed by further washing. The washing must be repeated until the resistance reaches the above figure. For accurate work the cell should be placed in a thermostat, the usual temperature being 25° C. The cell is now filled with a potassium chloride solution containing 0·1 gram-equivalent in 1 litre, and the resistance found. The conductivity of a $N/10$ potassium chloride solution is known (Table LXXXIII). The "cell constant" can now be calculated. The conductivity κ is connected with the resistance by the equation

$$\kappa = \frac{l}{aR},$$

where the symbols have the meanings given at the beginning of this paragraph. The cell constant is $\frac{l}{a}$, and is thus found by multiplying κ by R.

The cell is now thoroughly washed out, as before, filled with the solution under test, and the resistance again determined. If R' is the resistance, k the cell constant, then κ', the conductivity of the solution, is given by

$$\kappa' = \frac{k}{R'}.$$

TABLE LXXXIII.—CONDUCTIVITY OF $D/10$[1] POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES (Parker and Parker)

Temp., °C.	κ.
0°	0·007129
10°	0·009316
18°	0·011163
25°	0·012852

[1] The symbol $D/10$ stands for a concentration of one gram-equivalent in one cubic decimetre. The cubic decimetre is not exactly one litre, as at present defined, but is equal to 0·999973 litres. This arises from the fact that although the cubic centimetre was the original unit of volume, the litre has now been defined, not as 1,000 c.c., but as the volume of 1 kilogramme of pure, air-free water at the temperature of maximum density and under a pressure of 760 mm. This volume is not quite 1,000 c.c., but a little greater. In order to avoid confusion, many workers use the millilitre (ml.) instead of the cubic centimetre (c.c.) as a unit. Since the volume involved in our definition of equivalent conductivity is the c.c., we must use the cubic decimetre instead of the litre if very accurate results are necessary. In the experiment, as described above, it would not be necessary to make this correction, as there are other sources of error of greater magnitude.

The molecular and equivalent conductivities of the solution are found by multiplying the conductivity, κ', by the volume in c.cs. containing one gram-molecule, and one gram-equivalent respectively.

For very accurate work, solutions should be made up with specially purified water, known as conductivity water. It is not usually satisfactory to determine the resistance of the water and subtract it from the resistance of the solution. Kohlrausch and Heydweiller (1894) prepared very pure water by distilling it forty-two times, under reduced pressure. The water had a conductivity of $0{\cdot}043 \times 10^{-6}$ mhos.[1] It is a moot point whether this value has any real significance, as, by the process of distillation, the proportion of H_2^2O to H_2^1O in water is altered, and the composition of Kohlrausch and Heydweiller's specimen is not known.

For ordinary purposes conductivity water is prepared by distilling freshly distilled water with a small amount of potassium permanganate in a retort made of resistance glass, with a condenser of block-tin, or of resistance glass. Any corks used must be covered with tin-foil. Several stills have been devised for the routine preparation of conductivity water.

To illustrate the meaning of the terms an example may be taken. The resistance of a cell filled with $N/50$ potassium chloride at 25° C. was 550 ohms. The conductivity of $N/50$ KCl at this temperature is 0·002768. The cell was then washed out and filled with an $M/10$ solution of zinc sulphate at the above temperature. Its resistance was then 72·18 ohms. What are the molecular and equivalent conductivities of the zinc sulphate solution ?

The cell constant is first obtained. This is equal to the specific conductance of the KCl divided by the conductance measured. Conductance = 1/resistance, and for the solution of KCl = 1/550 reciprocal ohms, or mhos. Hence, the cell constant

$$k = 0{\cdot}002768/1/550 = 550 \times 0{\cdot}002768$$
$$= 1{\cdot}523.$$

The specific conductance of the zinc sulphate solution is therefore

$$\frac{1{\cdot}523}{72{\cdot}18} = 0{\cdot}02110.$$

The molecular conductivity is the conductivity multiplied by the volume in c.c. containing one gram-molecule, in this case 10 litres. Hence, the molecular conductivity is

$$0{\cdot}02110 \times 10{,}000 = 211{\cdot}0.$$

The equivalent conductivity is the conductivity multiplied by the volume containing one equivalent of the electrolyte. The equivalent

[1] The mho is the reciprocal ohm.

of zinc sulphate is one-half of the molecular weight. The volume containing this will be 5 litres, and so the equivalent conductivity is 105·5.

254. Variation of Conductivity with Dilution.—Although the actual conductivity of an electrolyte gets less as it is progressively diluted, yet it is found that the molecular and equivalent conductivities increase with dilution until a maximum limiting value is reached. Curves for a few typical substances are shown in Fig. 171. The figures for potassium chloride are given in Table LXXXIV. Note that the conductivity gets less, but the equivalent conductivity increases with increasing dilution.

TABLE LXXXIV.—CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTION AT 18° C.

Concentration gm.-equiv. per litre.	Volume containing 1 gm.-equiv. V c.c.	Conductivity. κ.	Equivalent Conductivity. $\Lambda = \kappa V$.	Apparent degree of Dissociation. $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.
0	∞	—	(129·9)	(1·00)
0·0001	10,000,000	0·00001291	129·1	0·994
0·001	1,000,000	0·0001273	127·3	0·980
0·01	100,000	0·001224	122·4	0·943
0·1	10,000	0·0112	112·0	0·862
1·0	1,000	0·0983	98·3	0·757

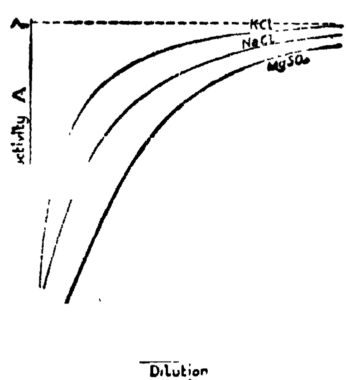


FIG. 171.—Showing the Form of the Conductivity-dilution Curve.

255. Degree of Dissociation.—The limiting value approached by the equivalent conductivity as the solution is diluted is called the *equivalent conductivity at infinite dilution*. The amount of current pass-

ing clearly depends upon the number of ions present in the solution, for they are the sole carriers of the current, and also upon their mobility, or the ease with which they get through the liquid. The two factors, then, upon which the conductance of a solution will depend are (*a*) the number of ions and (*b*) their mobility. Arrhenius assumed that the latter did not vary with dilution, and so the only reason for the increased equivalent conductivity must lie in the formation of more ions. At infinite dilution he supposed that the electrolyte was completely dissociated. Since the current flowing is proportional to the number of ions present, the amount of dissociation at any dilution will be given by

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}.$$

α is called the degree of dissociation of the electrolyte, and, of course, varies with the dilution. Λ_v is the equivalent conductivity at dilution v (*i.e.*, one gram-equivalent dissolved in v c.c. of solution), and Λ_∞ is that at infinite dilution. This is an extremely important relationship and will be frequently used in what follows.

It must be borne in mind that although all electrolytes give a value for α, it is now believed that strong electrolytes are completely dissociated at all dilutions, and that α for them represents the effect of interionic forces on the mobility of the ions. It is therefore called the "apparent degree of dissociation" for strong electrolytes (§ 274).

256. Effect of Dissociation on Osmotic Pressure and other Colligative Properties.—It has already been mentioned that the osmotic pressure laws do not apply to electrolytes, and that van't Hoff used the expression

$$PV = iRT$$

to take account of these anomalies (§ 246). It follows that i is equal to the ratio of calculated molecular weight to the observed value. It is found that the values of i are practically the same whether they are derived from osmotic pressure or freezing point observations. i varies with the dilution of the solution.

The fact that there is such a factor as i which must be introduced in the osmotic pressure equation to explain the observations means that the molecules may be broken down into smaller parts. The natural assumption to make, when the facts of electrolysis are known, is that these parts are the ions, and this is largely confirmed by the values of i obtained. Thus, for potassium chloride, the value is 1·88 ; for magnesium chloride it is 2·68, and for calcium nitrate it is 2·41, the dilution in all cases being 20 litres (*i.e.*, 1 gm.-equivalent is dissolved in 20 litres). It will be noted that for a substance which

splits into two ions (such as potassium chloride), the value of i approximates to 2, whilst for those which split into more than two ions it is greater than 2. The best proof of the connection between the phenomena of osmotic pressure and electrolysis is given by the fact that the degree of dissociation found from electrical conductivity agrees fairly well with that obtained from the osmotic pressure figures. If α is the degree of dissociation, then

$$i = (n - 1)\alpha + 1,$$

where n is the number of ions formed from one molecule of the electrolyte. The derivation of this equation is given in § 246 The figures in Table LXXXV. enable a comparison to be made.

TABLE LXXXV.—DEGREE OF DISSOCIATION FROM FREEZING POINT AND CONDUCTIVITY OBSERVATIONS

Substance.	Dilution. Volume in Litres containing 1 gm.-equiv.	i.	α from Freezing Point.	α from Conductivity.
Potassium chloride	200	1·96	0·96	0·97
$n = 2$	20	1·88	0·88	0·90
Potassium nitrate	200	1·96	0·96	0·95
$n = 2$	20	1·85	0·85	0·87
Hydrochloric acid	200	1·99	0·99	0·98
$n = 2$	10	1·91	0·91	0·92
Nitric acid	200	1·97	0·97	0·98
$n = 2$	5	1·87	0·87	0·92
Sodium hydroxide	200	1·99	0·99	0·96
$n = 2$	20	1·83	0·83	0·91
Calcium nitrate	20	2·41	0·70	0·73
$n = 3$	10	2·41	0·70	0·68
Potassium ferrocyanide	40	3·32	0·58	0·54
$n = 5$	10	2·79	0·45	0·46

The fact that the values of α obtained from conductivity and freezing point observations do not agree exactly for strong electrolytes points to the conclusion that the degree of dissociation for these substances is only apparent. As has been pointed out already, α is not a degree of dissociation for strong electrolytes, but a measure of the interionic forces (§ 274).

257. Conductivity and Viscosity.—Experiments have been carried out which indicate that there is an increase of resistance of the solution with increase in viscosity, the ions being hindered in their motion ; but this effect is not simply bound up with the viscosity. It has been supposed that the conductivity is inversely proportional to the viscosity, but it is probable that the law is nothing like so simple as this. If it were, there should be very little conductance through an electrolyte dispersed in a jelly, whereas the conductivity appears to suffer very little by this.

258. Effect of Temperature on Conductivity.—The conductivity of an electrolyte is increased much more than that of a metal by a given rise of temperature. The effect is probably due chiefly to alteration of the mobility of the ions, and not of their number. In turn, this variation of mobility may be affected by change in viscosity of the solution.

259. The Independent Mobility of Ions.—Kohlrausch, from a study of the equivalent conductivity of various electrolytes at infinite dilution, found certain relationships. Thus, if we take the two salts potassium chloride and nitrate, and compare their equivalent conductivities at infinite dilution with those of the corresponding sodium salts, we have

	Potassium.	Sodium.
Chloride . . .	130·10	108·99
Nitrate . . .	126·50	105·33

The value ($KCl - KNO_3$) = 3·60, whilst ($NaCl - NaNO_3$) = 3·66. ($KCl - NaCl$) = 21·11, and ($KNO_3 - NaNO_3$) = 21·17. Thus, the difference of two anions is constant, as is also the difference of two cations. This led Kohlrausch to state that the equivalent conductivity at infinite dilution was made up of two parts, that due to the anion and that due to the cation. If we have a salt such as silver nitrate, its equivalent conductivity at infinite dilution will be the sum of two terms, one due to the silver, and the other to the nitrate ion. These terms were called the "mobilities." The law is known as the Law of Independent Mobilities.

It is obvious that once one mobility is known (this can be obtained by a transport number experiment, § 261), all the rest can be obtained from the experimental values of Λ_∞ for different salts.

The values of some ionic mobilities are given in the Table.

TABLE LXXXVI.—IONIC MOBILITIES

Ion.	Mobility.	Ion.	Mobility.	Ion.	Mobility.	Ion.	Mobility.
Li	33·4	Cs	68	$C_2H_3O_2$	35	½ Cu	45·9
Na	43·4	H	313·9	OH	174	½ Cd	46·4
F	46·6	NH_4	64·3	NO_3	61·8	½ Sr	51·9
Ag	54·3	½ Mn	28	ClO_4	64	½ Ba	55·4
K	64·6	½ Co	43	½ Ni	44	½ Pb	60·8
Cl	65·5	SCN	56·7	½ $Fe^{\cdot\cdot}$	45	½ SO_4	68·5
Tl	65·9	IO_3	34·0	⅓ $Fe^{\cdot\cdot\cdot}$	61	½ CrO_4	72
I	66·25	ClO_3	54·87	⅓ $Cr^{\cdot\cdot\cdot}$	45	½ CO_3	60
Br	67·7	BrO_3	47·6	½ Mg	45·9	¼ $Fe(CN)_6''''$	95
Rb	67·5	IO_4	48	½ Zn	47·0	⅓ Al	40

By means of these values it is possible to calculate the equivalent conductivity of any electrolyte at infinite dilution. Thus, the value of the equivalent conductivity of potassium sulphate $\frac{1}{2}K_2SO_4$ at infinite dilution = 64·6 + 68·5 = 133·1.

The Table shows that the hydrogen and hydroxyl ions have much greater mobilities than any others. It must be remembered that these are not the absolute velocities of migration of the ions (§ 262).

The Law of Independent Mobilities is especially useful where the experimental determination of the conductivity at infinite dilution cannot be carried out with accuracy owing to the high value of the resistance. Thus, to find the conductivity of acetic acid at infinite dilution, we may determine that of hydrochloric acid, potassium acetate, and potassium chloride. In all these cases the experimental determination is possible, as the resistances are not too high. Then, if the Law of Independent Mobility of Ions is true,

$$\Lambda_\infty \text{ KCl} = [\text{K}] + [\text{Cl}],$$
$$\Lambda_\infty \text{ KAc} = [\text{K}] + [\text{Ac}],$$
$$\Lambda_\infty \text{ HCl} = [\text{H}] + [\text{Cl}],$$
$$\therefore\ [\text{H}] + [\text{Ac}] = [\text{H}] + [\text{Cl}] + [\text{K}] + [\text{Ac}] - \{[\text{K}] + [\text{Cl}]\}.$$
$$\text{or, } \Lambda_\infty \text{ HAc} = \Lambda_\infty \text{ HCl} + \Lambda_\infty \text{ KAc} - \Lambda_\infty \text{ KCl},$$

where symbols in square brackets denote mobilities.

260. Transport Numbers.—The fact that in electrolysis the ions move with different speeds causes changes in concentration round the electrodes. The way in which this change is connected with the speed of the ions is best shown by means of a diagram. In Fig. 172 the black dots represent anions and the circles cations. In a molecule the two may be supposed to be in conjunction.

We shall divide the solution into three compartments by means of imaginary partitions, *aa* and *bb*. The state of the solution before electrolysis may be represented by the line I. Here every anion is associated with a cation. This does not mean that dissociation has

not taken place, but since there is random motion, and there are exactly as many anions as cations, the probability is that an anion will find itself in the neighbourhood of a cation. Suppose that the ions move with the same speed; then whilst, say, two anions have crossed the partitions towards the anode, two cations will have crossed in the opposite direction towards the cathode. The state of the solution is shown in line II. Line III shows these ions liberated and also the fact that, though both anode and cathode compartments have become weaker, they have become so to the same extent.

Now suppose the anion moves twice as fast as the cation. Four

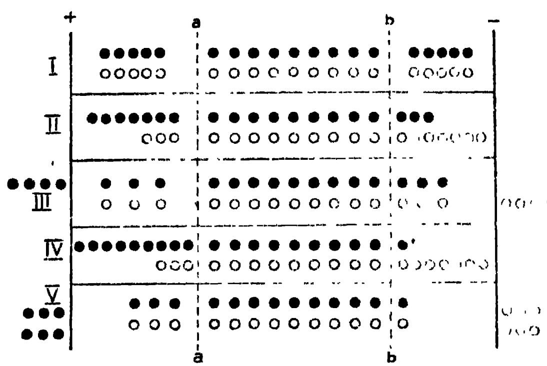


FIG. 172.—To illustrate Unequal Mobility of Ions.

anions will therefore pass across the partitions towards the anode, and only two cations will pass to the cathode. The state of the solution is now as in IV. After liberation of the ions at the electrodes, there are twice as many undischarged anions and cations in the anode compartment as there are in the cathode compartment. Thus, the fall of concentration at the anode divided by that at the cathode is equal to 1/2. Thus

$$\frac{\text{loss at anode}}{\text{loss at cathode}} = \frac{\text{speed of cation}}{\text{speed of anion}}.$$

It is useful to remember that the loss at any compartment is proportional to the speed of the ion which is leaving it. The student should convince himself of the truth of this statement by trying other relative speeds, such as 5/3. The remarkable fact that although the amounts of substance liberated at each pole are equivalent, yet one ion moves faster than the other, is thus accounted for.

Suppose that a fraction of the current n is carried by the anion;

then an amount $1 - n$ must be carried by the cation. Since the amounts of electricity carried are proportional to the speeds of the ions (§ 255), we have

$$\frac{\text{loss at anode}}{\text{loss at cathode}} = \frac{1-n}{n},$$

or, the value n is given by

$$n = \frac{\text{fall in concentration round cathode}}{\text{total fall round anode and cathode}}.$$

Hittorf, to whom the above reasoning is due, called n the transport

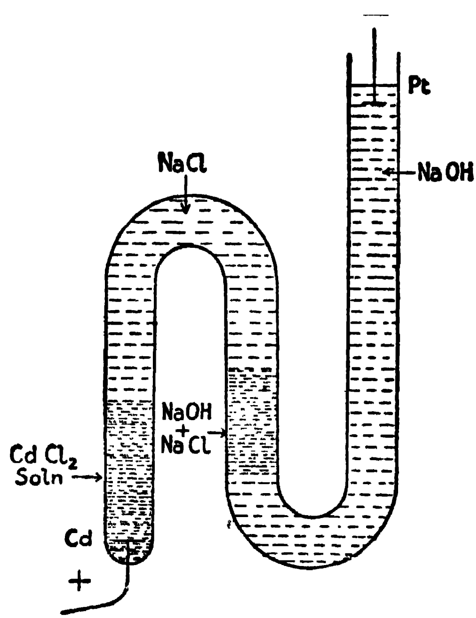


FIG. 173.—Hittorf's Transport Experiment.
[From *A Treatise on Physical Chemistry*, ed. H. S. Taylor (Macmillan).]

number of the ion. If n is the figure for the anion, then $1 - n$ must be that for the cation. If u is the velocity of the anion, and v that of the cation, then

$$\frac{n}{1-n} = \frac{\text{loss at cathode}}{\text{loss at anode}} = \frac{u}{v}.$$

261. Determination of Transport Numbers.—It was a condition of the above reasoning that the concentration in the middle compartment remained constant. Hence, in any experimental determination of transport numbers care must be taken that this is fulfilled.

Hittorf used the apparatus shown in Fig. 173. He used as electrolyte sodium chloride solution, and the anode was of cadmium, the cathode being of platinum. The action of the chlorine liberated at the anode produces cadmium chloride, and the cadmium ions move towards the cathode. Being much slower than the sodium ions, they never catch them up, and the cadmium chloride therefore remains as a separate layer. At the cathode all the chlorine ions have gone away, and are replaced by hydroxyl ions produced by the action of the sodium liberated there on the water. These ions are fairly fast, and therefore pass down into the solution, producing

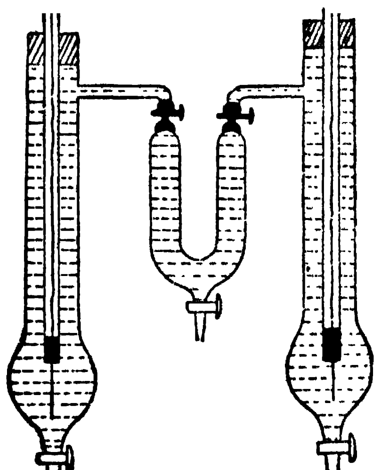


FIG. 174.—Transport Number Tube.

mixing. A similar apparatus is shown in Fig. 174. Here the three portions are tapped and can be run off for analysis without disturbing the rest.

The following are some results of the Hittorf experiment, and are given to show the method of calculation.

The original solution contained 0·01784 per cent. chlorine, the weights of chlorine in the three parts of the apparatus before and after electrolysis being

	Before.	After.
Anode part	0·04048 gm.	0·04671 gm.
Central part	0·03482 „	0·03483 „
Cathode part	0·05913 „	0·05289 „

Note that the composition of the central part remained unchanged, within the limits of experimental error.

The weight of silver deposited in a silver voltameter connected in series with the transport number tube was equivalent to 0·01021 gm. chlorine.

From the above data, the gain in the anode part was 0·00623 gm., whilst the loss in the cathode part was 0·00624 gm.

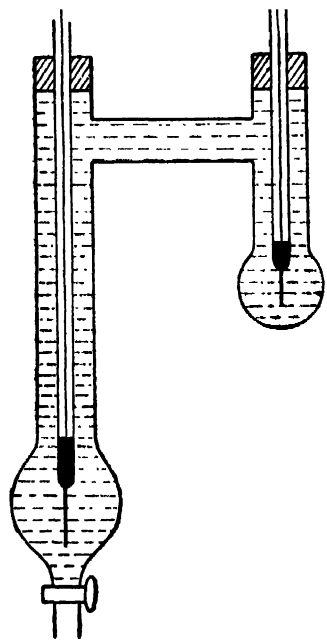


FIG. 175.—Transport Number Tube.

The transport number of Cl^- in the electrolyte is therefore

$$\frac{\text{loss round cathode}}{\text{total loss}}$$

$$\frac{0{\cdot}00624}{0{\cdot}01021} = 0{\cdot}611.$$

The transport number of the sodium ion is therefore 0·389.

The common form of transport number tube used in elementary work is shown in Fig. 175. Suppose it is to be used in the determination of the transport numbers of the silver and nitrate ions in silver nitrate solution. Suppose that both electrodes are of platinum, and that the solution of silver nitrate has deposited on the cathode, during the electrolysis, 1·2591 gms. of metallic silver. A certain volume of the solution taken from the region of the anode now

contains 12·5533 gms. of silver, whereas before it contained 13·1426 gms. The solution at the anode has therefore lost 0·5893 gm. of metal. The total loss is 1·2591 gms. of silver. Hence, the transport number of the cation

$$n = \frac{\text{loss round anode}}{\text{total loss}},$$
$$= \frac{0\cdot5893}{1\cdot2591} = 0\cdot457.$$

The transport number of the anion is therefore 1 − 0·457 = 0·543.

In some forms of the apparatus the anode is of silver. In this case a silver voltameter must be connected in the circuit, but the calculation is of similar form to the above.

TABLE LXXXVII.—TRANSPORT NUMBERS OF ANIONS OF SALTS IN $M/10$ SOLUTION AT 18° C.

Salt.	Transport Number of Anion.	Salt.	Transport Number of Anion.
KCl	0·508	$AgNO_3$	0·528
KBr	0·508	KOH	0·735
NH_4Cl	0·508	HCl	0·172
KI	0·508	$\frac{1}{2}BaCl_2$	0·585
NaCl	0·617	$\frac{1}{2}CdI_2$	0·71
LiCl	0·69	$\frac{1}{2}CuSO_4$	0·632
KNO_3	0·497		

The arrangement of apparatus for carrying out a determination of the transport numbers of the silver and nitrate ions is shown in Fig. 176. Suppose the transport number tube is fitted with a silver anode, and a platinum cathode. V is a silver voltameter, made by placing two pieces of platinum foil, mounted on platinum wires, in silver nitrate solution. A solution containing 17 gms. of silver nitrate in 1,000 *gms.* of water is made up, and 100 gms. of this solution are weighed into the voltameter. The transport apparatus is filled with the silver nitrate solution. A small current is required for this experiment. A 50-volt battery is convenient; if not available, a suitable resistance may be placed in the mains (which must be direct current, not alternating). The current is passed for about five hours. Whilst the electrolysis is proceeding, two 50-gm. lots of the silver nitrate solution are weighed out and titrated against standard potassium thiocyanate ($N/10$). When the experiment is finished, about as much liquid as would fill the anode

limb is run off from the transport apparatus into a weighed flask, and weighed. It is then titrated with $N/10$ potassium thiocyanate. The silver solution from the voltameter is also titrated. From these results the required transport numbers can be obtained.

To show the method of calculation, let the 50 gms. of silver nitrate solution started with require x c.c. of $N/10$ potassium thiocyanate. The titre of the solution in the voltameter at first would therefore be $2x$.

Let its titre at the end of the experiment be y c.c. Then the amount of current passed is proportional to $2x - y$.

The anode solution weighs w gms. and requires z c.c. of thiocyanate. But, an amount of silver proportional to $2x - y$ c.c. of thiocyanate has been dissolved from the anode by the passage of the current. Hence, the amount of the original silver nitrate left is proportional to $z - (2x - y)$.

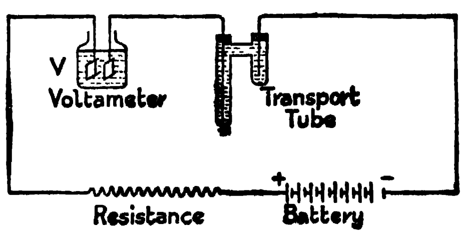


FIG. 176.—Apparatus for determining Transport Numbers.

The silver nitrate originally present in w gms. of solution corresponds to $wx/50$ c.c. potassium thiocyanate. Hence, loss of silver from anode is proportional to $(wx/50) - z + 2x - y$ c.c. potassium thiocyanate. Hence, transport number for the cation (silver)

$$= \frac{\text{loss at anode}}{\text{total loss}},$$

$$= \frac{(wx/50) - z + 2x - y}{2x - y}.$$

262. Absolute Velocity of Ions.—The ionic mobilities of Kohlrausch are not the absolute velocities of the ions. These may be obtained as follows: In determining absolute velocity of ions it is clear that the speed will depend on the potential gradient in the solution. It is therefore necessary to specify this, and the absolute velocity is measured in cm. per sec. for a potential gradient of 1 volt per cm.

Consider the solution in a centimetre cube, the electrodes being at the shaded faces. Let there be a potential of 1 volt between them. The current flowing through the cell will then be numerically

equal to the specific conductivity, κ (by definition), and will be in ampères. Let the concentration be c, and let it be so small that the solution may be assumed to be completely ionised. The amount of electricity passing through the cube in one second will be

$$\kappa = c\Lambda_\infty = c(u + v),$$

where u is the ionic mobility of the anion, and v is that of the cation (§ 259).

Let U and V be the absolute velocities of the anions and the

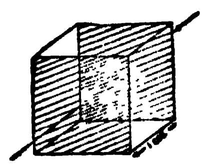


FIG. 177.

cations respectively. All the anions within a distance U cm. of the anode will have moved up to it in one second, and all cations within a distance V cm. from the cathode will have moved up to it in one second. These correspond to Uc and Vc gm.-equivalents respectively, since 1 c.c. contains c gm.-equivalents. They will involve

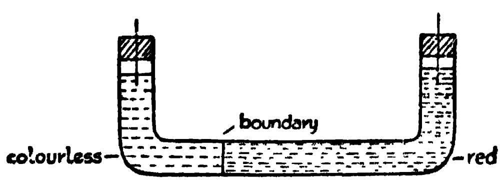


FIG. 178.—Lodge's Tube.

the transfer of $96{,}500(U + V)c$ coulombs (from Faraday's Second Law, § 249).

Hence, $$96{,}500(U + V)c = c(u + v).$$

Since $$\Lambda_\infty = u + v,$$

$$U = \frac{u}{96{,}500}, \text{ and } V = \frac{v}{96{,}500}.$$

The absolute velocities of the ions are therefore obtained by dividing the ionic mobilities by 96,500. Thus, the ionic mobility of the hydrogen ion is 313·9, hence, its absolute velocity is 313·9/96,500

= 0·00325 cm. per sec. for a potential gradient of 1 volt per cm.

The absolute velocities of the ions are much smaller than one would suppose. The fastest of them, the hydrogen ion, thus moves only with a velocity of 0·00325 cm. per sec., under a potential gradient of 1 volt.

The actual velocity of the ions can be observed by Lodge's moving boundary method. A tube of the form shown in Fig. 178 is filled with a jelly of agar-agar, phenolphthalein being added, and the whole being coloured red by the addition of a trace of alkali during the preparation of the jelly. When the jelly has set, sodium sulphate solution is added to one side, and dilute sulphuric acid to the other. On passing the current, hydrogen ions pass along the solution, and their rate of motion can be followed by noting the progressive loss of colour of the jelly, owing to the neutralisation of the base by the hydrogen ions. The value for the hydrogen ion obtained by Lodge was 0·0025 cm./sec.

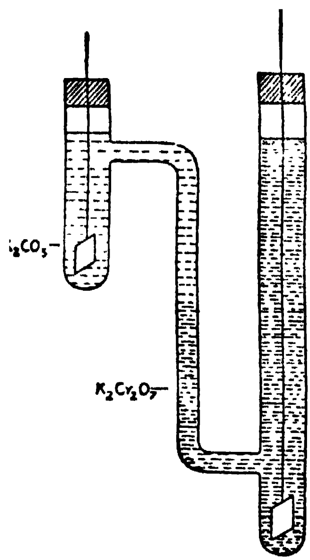


FIG. 179.—Whetham's Apparatus.

The method was improved by Whetham, who used two solutions with a common ion of the same concentration and almost the same conductance. One of these was coloured and the other not. The substances chosen were potassium dichromate and potassium carbonate. The apparatus used is shown in Fig. 179. The coloured ion moved, and its rate of motion could be followed by noting the position of the boundary. The current was measured, and from the results the absolute mobilities were obtained, the results agreeing with those of Kohlrausch.

The study of transport numbers has indicated the existence of hydration of the ions. If the transport numbers of the alkali metal ions are determined in $N/20$ solutions of the chlorides at 18° C., the values given in Table LXXXVIII are obtained (Glasstone).[1]

It would be expected that the lightest ion would have the greatest mobility, but this is not the case. As far back as 1894 Bredig suggested that this might be due to hydration of the ions. If the ions were attached to water molecules, their size would be consider-

[1] S. Glasstone, "The Electrochemistry of Solutions" (Methuen).

TABLE LXXXVIII

Metal.	Transport Number.	Atomic Volume.
Li	0·320	11·8
Na	0·386	23·7
K	0·496	45·3
Rb	0·485	56·0
Cs	0·492	70·7

ably increased. If this is so, the lithium ion must be heavily hydrated, and that of cæsium very little. This is confirmed when the salts of these metals are considered, for in the crystalline state the salts are completely ionised. Thus, lithium salts are mostly hydrated, those of sodium frequently hydrated, whilst the number of hydrated salts met with decreases as the series is ascended. This view also follows from the electronic theory of valency (§ 171).

If an indifferent substance such as sugar is added to an electrolyte, the changes of concentration of this substance at the electrodes will depend on the transport numbers of the ions, and also upon the amounts of water which each ion carries. If a and b are the number of water molecules attached to each anion and cation respectively, then

$$na - (1 - n)b = x$$

is the amount of water molecules transported to the electrode per Faraday, n being the transport number of the anion. Experiments carried out in this way show that nearly all ions are hydrated. Reference to this will again be made on p. 594. Evidence for hydration of ions also comes from freezing point observations. In strong solutions, the ions remove a certain amount of water from the solvent, and thus the solution appears to be stronger. In this way Jones was able to find the degree of hydration of various ions.

Hydration of ions must be considered as a type of compound formation, and as such it should be governed by the electronic theory of valency. It is known that water is both an acceptor and a donor, and hence it will be very likely to co-ordinate with other substances. The hydrogen atom will co-ordinate with other bodies to make up its number of electrons to four; it is to be expected, then, that the hydrogen ion will co-ordinate even more easily. Its combination with water is therefore not surprising.

263. Determination of Transport Numbers from Electromotive Force Measurements.—The e.m.f. of a concentration cell of the type

$$Ag \mid AgNO_3 \mid AgNO_3 \mid Ag$$

where c_1 and c_2 are concentrations, involves the transport number of the anion. The determination can therefore be used to find transport numbers. The method is described on p. 652.

264. Non-aqueous Solutions.—The study of solutions in solvents other than water has provided a considerable amount of information on the nature of electrolysis. The ions are all solvated to a certain extent in water, whereas in non-aqueous solvents this might not be the case.

It is not an easy matter to study non-aqueous solutions, as the presence of even a trace of water may seriously alter the results. The chief work has been done by Walden,[1] who employed in many of his experiments the compound tetraethylammonium iodide $N(C_2H_5)_4I$, dissolved in various solvents. He discovered that the equivalent conductivity at infinite dilution of a salt is inversely proportional to the square root of its molecular weight and to the viscosity of the solvent.

Amongst the solvents used, those containing hydroxyl groups, such as methyl and ethyl alcohols, behave in a similar manner to water. The mobility of ions in various solvents has been found; the following are some of the results :—

	Water.	Methyl Alcohol.	Ethyl Alcohol.	Acetone.	Nitromethane.
H^+ .	351	142	59·5	88	63
NH_4^+ .	74	58	19	98	64
K^+ .	74	54	22	82	60
Ag^+ .	63	50	17·5	90	53

It is seen that the hydrogen ion has a greater mobility in the hydroxylic solvents (with the exception of ethyl alcohol) than in the others. This may be due to the hydrogen ion being carried from a $[H_3O]^+$ ion to a water molecule, much as in the Grotthus chain explanation (§ 248), so that the calculated velocity is not that of the hydrogen ion itself, but the total effect of a number of hydrogen ions.[2] Goldschmidt has shown that the addition of a trace of water to an ethyl alcoholic solution of hydrogen chloride reduces the equivalent conductivity considerably, so that the hydration of the hydrogen ion which results must prevent it from taking part in this chain method of transference.

[1] A great deal of the more modern work has been done by Hartley and his co-workers at Oxford.

[2] Hückel, *Z. Electrochem.*, 1928, **34**, 546. An account of the work done on this subject is to be found in the various volumes of *Annual Reports*, published by the Chemical Society, and particularly in the volume for 1930.

265. Effect of Dielectric Constant on Ionisation.—Walden showed that a dissolved salt gives a definite value for the ratio $\frac{\Lambda}{\Lambda_\infty}$ at a dilution which is inversely proportional to the cube of the dielectric constant of the solvent. Thus, if we choose $\frac{\Lambda}{\Lambda_\infty} = 0{\cdot}5$, we shall find the dilution required to give this is inversely proportional to the cube of the dielectric constant. Some data are given in Table LXXXIX. The ratio $\frac{\Lambda}{\Lambda_\infty}$ is 0·5. This relationship is only approximately true, and reaches this degree of accuracy only for strong electrolytes.

TABLE LXXXIX.—ELECTROLYTIC DISSOCIATION AND DIELECTRIC CONSTANT (25° C.)

	Dielectric Const., D.	Dilution, v.	$D(v)^{\frac{1}{3}}$ (nearest integer).
Silver nitrate in water . .	81	0·7	72
Sodium chloride in formic acid .	62	2·1	79
Tetraethylammonium iodide in furfurol	42	5·0	72
Potassium iodide in acetonitrile .	36·4	11·0	81
Lithium nitrate in methyl alcohol.	35·4	9·0	74
Lithium chloride in ethyl alcohol .	26·8	35	88
Potassium iodide in acetone .	21·2	60	83

It is found that only in liquids of fairly high dielectric constant can ionisation take place. The dielectric constant of a substance is dependent upon its dipole moment, *i.e.*, upon the degree of asymmetry of the arrangement of charges in the molecule (§ 382). It is not surprising therefore to find that those with high dielectric constants, *i.e.*, very unsymmetrical fields, can bring about ionisation.

The actual mechanism of ionisation in solution, where it is known that the solid salt was not completely ionised before solution, cannot be said to be known. Many hold the view that compound formation with the solvent is a necessary preliminary to further breakdown into ions.

The behaviour of salts in non-aqueous solvents is usually considerably different from that in water. Ionisation in any solvent is governed largely by Fajans' theory (p. 169). This states that ionisation will be promoted by the presence of a small anion and a large cation.

266. Degree of Dissociation in Non-aqueous Solvents.—Walden has found that the degree of dissociation of a dissolved salt is approximately constant for saturated solutions of substances in any solvent provided that water is rigidly excluded. The ratio of $\frac{\Lambda_v}{\Lambda_\infty}$ is given in Table XC for saturated solutions of tetraethylammonium iodide in various solvents. The constancy is remarkable.

TABLE XC.—DISSOCIATION OF NEt_4I IN SATURATED SOLUTIONS AT 25° C.

Solvent.	Λ_v.	Λ_∞.	$\frac{\Lambda_v}{\Lambda_\infty}$
Methyl alcohol . .	47·85	124	0·40
Furfurol . . .	26·83	50	0·52
Acetonitrile . .	96·4	200	0·48
Acetone . . .	112·0	225	0·50
Ethyl nitrite . .	68·67	140	0·49

By an examination of the equivalent conductivities of the thiocyanates and perchlorates of lithium, sodium, potassium and ammonium, in nitromethane at various dilutions, Wright, Murray-Rust and Hartley found that the empirical relationship

$$\Lambda_v = \Lambda_\infty - xc^{\frac{2}{3}}$$

was true. In this equation c is the concentration and x a constant. Salts of the tetraethylammonium radical, however, behave according to the equation

$$\Lambda_v = \Lambda_\infty - x\sqrt{c}.$$

267. Evidence in Favour of the Dissociation Theory.—(1) The reactions of salts in inorganic chemistry show that salts are made up of two parts. Thus, all chlorides give the same reactions, whereas there are also reactions common to all potassium salts.

(2) Various physical properties of solutions of electrolytes are additive. Thus, surface tension, and density, may be regarded as the sum of three separate factors, one characteristic of the solvent, another of the cation, and the other of the anion.

(3) The heat of neutralisation of a strong acid by a strong base is a constant (§ 278).

(4) The colours of solutions at high dilution should be made up of that of the solvent and that due to the two ions. If the solvent is colourless, and one ion is colourless and the other coloured, the

substances falling into this class should all possess the same colour. Thus permanganates have been shown all to possess the same absorption spectrum.

(5) The theory explains in a simple manner the anomalies in osmotic pressure, depression of the freezing point, and elevation of the boiling point shown by electrolytes (§ 256).

(6) X-ray analysis indicates that ions are present in some solids (§ 125).

(7) Ostwald's Dilution Law is obeyed fairly closely by weak electrolytes (§ 271).

(8) The theory explains precipitation, through the theory of the solubility product (§ 288).

(9) Dissociation is shown in certain experiments on the distribution coefficient (p. 548).

268. The Theory of Metallic Conduction.—The chief difference between metallic and electrolytic conduction lies in the fact that there is no decomposition or polarisation in the former. The current passes through the conductor without bringing about any chemical change. There are also other differences. The temperature variation of resistance is different in the two cases. In the case of a metal there is a minimum resistance at some definite temperature, whilst for electrolytes the resistance decreases continuously with increase of temperature. The spectra of the two classes of substances are different. Electrolytic conductors show selective absorption and emission in the ultra-violet and the infra-red, whilst the corresponding spectra in the case of metallic conductors are continuous.

The generally accepted theory is that the flow of the current in a metal is merely the flow of electrons, the positive ions being stationary. Various experiments have led to this conclusion, but they cannot be studied here. Drude, assuming that the electrons in a metallic conductor could be regarded as if they were gas molecules on the kinetic theory, obtained an expression for the conductivity of a metal,

$$\kappa = \frac{e^2Nl}{2mv},$$

where e is the charge on the electron, N the number of molecules per unit volume, l the mean free path of the electron, m the mass of the electron and v its velocity. Assuming equipartition of energy, as in the kinetic theory of gases (p. 191), we can replace $\frac{1}{2}mv^2$ by $\frac{3}{2}kT$, where k is Boltzmann's constant, and T the absolute temperature. Thus

$$\kappa = e^2Nlv/6kT.$$

The thermal conductivity of a metal is also intimately related to the electrical conductivity, a fact which is shown qualitatively by the order of these two properties in a series of metals being approximately the same. A good electrical conductor is also a good heat conductor. Drude calculated that the thermal conductivity was given by

$$\theta = \tfrac{1}{2}Nklv.$$

Dividing thermal by electrical conductivity, we have

$$\frac{\theta}{\kappa} = \frac{3k^2T}{e^2} = T \times \text{const.},$$

which is known as the law of Wiedemann and Franz.

Some crystals, which consist of ions regularly spaced in a lattice (*e.g.*, sodium chloride), show this electronic type of conduction to a very small extent. When a point electrode is inserted at the surface of a crystal of sodium chloride, and a high potential is applied between it and an electrode elsewhere in the crystal, a small current flows, and a coloration of the crystal occurs in the neighbourhood of the point electrode. The colour varies with the temperature and nature of the crystal. Now it is known that the opacity of the metals is due to the fact that electrons are free in the space lattice of the crystal. The metal crystal lattice probably consists of a number of positive ions in the regular lattice, with a cloud of free electrons associated with the lattice, but not fixed. These are sometimes called "electron gas." They are the electrons which move through the metal when an external e.m.f. is applied. When, therefore, a coloration is observed in the neighbourhood of the electrode in the salt crystal, it is inferred that in this region there is electron gas. There are, however, some differences between this conduction by a salt and metallic conduction, for there is also electrolytic conduction in a solid salt.

269. Conductivity of Alloys.—If there is no chemical combination between the constituents of an alloy, and if there is no formation of solid solutions, the conductivity of an alloy is the sum of the conductivities of the constituents, according to their proportions. This is known as the mixture rule. When solid solutions are formed, the resistance is considerably greater than that predicted by the mixture rule.

A study of the conductivity of alloys is useful in determining their nature. If the graph drawn between electrical conductivity and composition is a straight line it may be inferred that the components are not miscible. If a solid solution is formed, the conductivity-composition curve shows a flat minimum and falls rapidly at both ends from the values for the pure components (Fig. 180). There

may be combinations of these two types, one part of the curve being linear, whilst the other shows a minimum. This shows that there is a limited concentration range where there is miscibility. The nature of the curve will also show whether chemical compounds are formed. If there is a sharp point on a curve, it indicates the existence of a chemical compound, but the reverse is not always true.

270. Effect of Temperature on Conductivity of Metals.—The general formula connecting the resistance (R) of a pure metal with temperature is

$$R = a + bT + cT^2,$$

where a, b, and c are constants, and T is the absolute temperature. The value of c is very small, so for small temperature ranges the third term may be neglected.

This expression has been made use of for determining temperatures by the platinum resistance thermometer, an excellent method of measuring both high and low temperatures.

The above expression only holds for ordinary temperatures. When the temperature is reduced so much that it is in the neighbourhood of the absolute zero, some metals are found to become super-conducting. Their resistance falls practically to zero, and a current once started in a closed ring of metal will go on flowing for a long while. The investigation (which is still proceeding) of this state has been done largely at Leyden. Certain metals have been found not to become super-conducting, but the resistance falls to a minimum and then rises again. Examples of this class are copper and platinum.

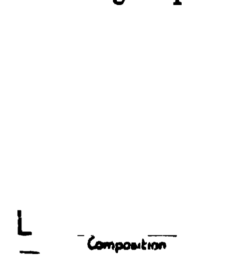


FIG. 180.—Conductivity Curve for Alloy forming Solid Solution.

The existence of the super-conducting state shows that, at very low temperatures, the motion of the "electron-gas" (§ 268) through the metal is not hindered. There can be no interaction between the electrons and the positive ions. As the temperature increases, the phenomenon of resistance comes into play. This must be due to a friction-like, or viscosity, force exerted on the electrons, presumably by the positive ions.

SUMMARY

All electrical conduction is one of two types :—

(1) Electronic conduction. The flow of current is the motion of electrons through the medium. This type is found in metallic conduction ; and

(2) "Carrier" conduction. The current is borne through the

medium by material bodies, which carry the electrons. These bodies may be atoms, molecules, dust, etc. In electrolytic conduction the electrons are carried by atoms or molecules.

When an electrolyte is dissolved in water it immediately breaks up, at least partially, into ions, which are charged atoms or groups. When electrodes, connected to a battery, are placed in the solution, the ions wander to the electrode of opposite charge, and are there discharged and liberated. They may be separated, or there may be further ("secondary") reactions with the solvent or solute. Faraday's Laws of Electrolysis state that (1) the amount of decomposition caused in electrolysis is proportional to the quantity of current passed, and (2) for the same quantity of electricity passed through different solutions, the amount of decomposition is proportional to the equivalent of the element, or group, deposited.

According to Arrhenius, the extent of dissociation of an electrolyte into its ions depends upon the concentration of the solution. The degree of dissociation (α) is the fraction of the electrolyte dissociated.

The specific resistance of a conductor is the resistance of a specimen of the material of length 1 cm. and 1 sq. cm. area of cross-section. The reciprocal of the specific resistance is the conductivity. The molecular conductivity, μ, is the conductivity multiplied by the volume in c.c. containing one gram-molecule of the electrolyte. The equivalent conductivity, Λ, is the conductivity multiplied by the volume in c.c. containing one gram-equivalent of the electrolyte. The degree of dissociation is given by $\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$, where Λ_v is the equivalent conductivity at dilution v, and Λ_∞ is that at infinite dilution.

The fact that electrolytes are dissociated causes anomalies in the colligative properties of these substances (osmotic pressure, depression of vapour pressure and freezing point, and elevation of boiling point), since these properties are dependent upon the number of individual particles present in the solution. They afford other methods of finding α, values of which agree, in general, with those obtained by the conductivity method.

The ions in an electrolyte move independently of each other, and with different velocities. The fraction of the current carried by any particular ion is called its "transport number." The absolute velocity of the ions is small, and has been observed directly.

Results of conductivity measurements in non-aqueous solvents indicate that this depends upon the viscosity and dielectric constant of the solvent.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 33.—Determine the conductivity of a solution of copper sulphate, and calculate its molecular and equivalent conductivities (§ 253).

Experiment 34.—Determine the variation of equivalent conductivity of copper sulphate with temperature.

Repeat the above experiment, placing the cell in baths of various temperatures. Plot the equivalent conductivity against temperature.

Experiment 35.—Determine the transport numbers of the silver and nitrate ions (§ 261).

SUGGESTIONS FOR FURTHER PRACTICAL WORK

(1) Determine the transport numbers of sodium and chloride ions in a solution of common salt.

(2) Determine whether transport number varies with dilution or temperature.

(3) Carry out transport experiments with non-aqueous solvents.

SUGGESTIONS FOR FURTHER READING

DAVIES, C. W. "The Conductivity of Solutions." (*Chapman and Hall*, 1930.)

GLASSTONE, S. "Electrochemistry of Solutions." (*Methuen*, 1930.)

HARTLEY, H., and others. "Electrical Conductivity of Solutions." (Report in "Annual Reports on the Progress of Chemistry," issued by the Chemical Society, 1930.)

PARTINGTON, J. R. "Conductance, Ionization and Ionic Equilibria," Chapter XI. of Vol. I. of "A Treatise on Physical Chemistry," ed. H. S. Taylor. (*Macmillan*, 1924.)

QUESTIONS

(1) State Faraday's Laws of Electrolysis. How may they be verified?

(2) Explain what takes place when an electric current is passed successively through solutions of copper sulphate, silver nitrate, lead acetate and sodium chloride, the electrodes being of platinum. What is the relationship between the quantities of substances liberated?

(3) What is meant by the term "degree of dissociation"? How may it be determined?

(4) How is it possible to determine the equivalent conductivity of acetic acid at infinite dilution?

(5) In what way does the electrical conductivity of a solution vary with dilution? How can the variation be explained?

(6) What is meant by the term "ionic mobility"? How may the ionic mobilities be determined, and of what use are they?

(7) How may the actual mobility of the hydrogen ion be demonstrated?

(8) When an electric current is passed through a solution of zinc chloride between carbon electrodes, a certain minimum potential is necessary to effect decomposition. Why is this?

(9) Calculate the osmotic pressure of an $M/10$ solution of urea, $CO(NH_2)_2$ at 0° C. Why is it that the osmotic pressure of a solution of potassium chloride is almost twice as great as this?

(10) A 1 per cent. solution of sodium chloride freezes at − 0·604° C. The molecular depression for water is 18·5° (100 gms.). Calculate the degree of dissociation of the sodium chloride.

(11) What is meant by the transport number of an ion? How may it be determined?

In a transport number experiment a solution of silver nitrate containing 0·0074 gm. per gram of water was used. During the experiment 0·0785 gm. of silver was deposited in a silver voltameter placed in series

with the transport apparatus. After the experiment, 25 gms. of the anode solution contained 0·2553 gm. of silver nitrate. Find the transport numbers of the silver and nitrate ions. The electrodes were of silver.

(12) The velocity of migration of the silver ion at 18° C. is 0·000577 cm. per sec., and that of the nitrate ion 0·000630 cm. per sec. What is the specific conductance of a 0·1 M silver nitrate solution if the van't Hoff i factor is 1·5? All observations are made at the same temperature.

(13) Discuss the results of conductivity work in non-aqueous solutions.

(14) In what ways does a knowledge of the electrical conductivity of an alloy give information as to its nature?

(15) Nernst and Loeb. in determining the transport numbers of the silver and nitrate ions, found the following results: Before the experiment, 1 gm. of the anode solution contained 0·001788 gm. of silver nitrate. After the experiment 20·09 gms. of solution taken from the anode compartment contained 0·06227 gm. of silver nitrate. 0·0322 gm. of silver was deposited in a voltameter placed in the circuit. Calculate the transport numbers of the silver and nitrate ions.

(16) The osmotic pressures of solutions of potassium nitrate, at 15° C., are given in the following table:—

Conc. (%)	Pressure (cms.)
0·80	130·4
1·43	218·5
3·3	436·8

Calculate the apparent molecular weight of potassium nitrate from each of these observations, and explain the results.

CHAPTER XIII

IONIC EQUILIBRIA

271. The Ostwald Dilution Law.—In a solution of a binary electrolyte there will be an equilibrium between the ions and the undissociated molecule, if the Arrhenius hypothesis is correct.[1] Thus, we have

$$AB \rightleftharpoons A^+ + B^-.$$

It is therefore to be expected that the Law of Mass Action can be applied to this equilibrium just as it can to ordinary homogeneous equilibria. This application was first carried out by Ostwald (1888), and the result is known as *Ostwald's Dilution Law.*

Suppose that originally one gram-molecule of the binary electrolyte AB is dissolved in v litres of water, and that its degree of dissociation is α. Then

$$AB \rightleftharpoons A^+ + B^-.$$

The quantities present at equilibrium are $\frac{1-\alpha}{v}$ of AB, $\frac{\alpha}{v}$ of A^+, and $\frac{\alpha}{v}$ of B^-.

Applying the Law of Mass Action,

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1-\alpha}{v}} = K,$$

$$\frac{\quad}{v(1-\alpha)} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This is known as the Dilution Law.

If α is small compared with unity, it can be neglected in the denominator of the left-hand side of equation (1). In this case,

$$\frac{\alpha^2}{v} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\alpha = \sqrt{Kv}.$$

K is called the "*dissociation constant*"[2] of the substance. It is

[1] This excludes strong electrolytes which, as will be shown later, do not obey the Ostwald Dilution Law.

[2] K is also sometimes called the "affinity constant."

seen that, in the case of a weak electrolyte (*i.e.*, α is small), the degree of dissociation is at a given concentration proportional to the square root of the dissociation constant.

The Law has been applied mainly to acids and bases. It is clear that the value of K will be a good measure of the strength of an acid, which is supposed to depend on the concentration of hydrogen ions in its solution (§ 293), for, as shown above, the degree of dissociation at a given concentration is proportional to the square root of K. A strong acid will be one with a large value for K in solutions of moderate concentration.

It is well to notice that the assumptions that are made in the derivation of this Law are that the Law of Mass Action applies to charged ions, and, even more fundamentally, that the Arrhenius hypothesis of electrolytic dissociation is true.

The Ostwald Dilution Law can be obtained in another form by substituting the value of $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ in the equation (1) above. This gives

$$K = \frac{\Lambda_v^2}{v\Lambda_\infty(\Lambda_\infty - \Lambda_v)}$$

The above formula would apply, of course, to a monobasic acid, such as acetic acid. Dibasic acids, however, ionise in two stages, and therefore possess two dissociation constants :—

First dissociation : $H_2A \rightleftharpoons H^+ + HA^-$.
Second dissociation : $HA^- \rightleftharpoons H^+ + A^{--}$.

The two dissociation constants are :—

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]},$$

and

$$K_2 = \frac{[H^+][A^{--}]}{[HA^-]}.$$

As a rule, for dilutions up to about 2,000 litres, the second stage is negligible. Thus, with hydrogen sulphide,

$$\frac{[H^+][HS^-]}{[H_2S]} = 10^{-7},$$

and

$$\frac{[H^+][S^{--}]}{[HS^-]} = 10^{-15}.$$

272. Experimental Verification of the Dilution Law.—To test the law experimentally it is necessary to determine the degree of dissociation of a binary electrolyte at various dilutions, and then substitute the values of v and α in the Ostwald equation, and see if a constant is obtained.

The degree of dissociation is best determined by conductivity observations. α is connected with the equivalent conductivity and that at infinite dilution by the equation

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty},$$

where Λ_v is the conductivity at dilution v, and Λ_∞ is that at infinite dilution (§ 255).

For the sake of example, suppose it is necessary to see whether Ostwald's Dilution Law holds for a weak acid such as propionic acid. The conductivity is determined at various dilutions by the ordinary method (see p. 512). It is now necessary to find the equivalent conductivity at infinite dilution. As propionic acid is weak, it does not conduct well, with the result that the resistance of a very dilute solution is too great to be measured with accuracy. It is therefore necessary to apply Kohlrausch's method, which regards the equivalent conductivity at infinite dilution as made up of two parts, one due to the anion and the other due to the cation (§ 259). It is possible to determine the equivalent conductivity at infinite dilution of potassium propionate, potassium chloride and hydrochloric acid. If the quantities in square brackets represent the portion of the equivalent conductivity at infinite dilution due to the ions stated therein, we have

$$\underbrace{[\mathrm{H}] + [\mathrm{Pr}]} = \underbrace{[\mathrm{K}] + [\mathrm{Pr}]} + \underbrace{[\mathrm{H}] + [\mathrm{Cl}]} - \underbrace{[\mathrm{K}] - [\mathrm{Cl}]}.$$

Thus, the conductivity of propionic acid at infinite dilution is

TABLE XCI.—IONISATION OF ACETIC ACID IN AQUEOUS SOLUTION AT 25° C.

$\Lambda_\infty = 387{\cdot}9.$

v.	Λ_v	α.	$K = \frac{\alpha^2}{v(1-\alpha)}$
0·334	0·6186	0·001595	$7{\cdot}7 \times 10^{-6}$
0·672	1·123	0·002896	$12{\cdot}5 \times 10^{-6}$
0·989	1·443	0·003636	$14{\cdot}0 \times 10^{-6}$
1·977	2·211	0·005701	$16{\cdot}5 \times 10^{-6}$
5·374	3·804	0·009806	$18{\cdot}1 \times 10^{-6}$
10·753	5·361	0·01382	$18{\cdot}0 \times 10^{-6}$
24·875	8·388	0·02163	$19{\cdot}2 \times 10^{-6}$
63·26	13·03	0·03359	$18{\cdot}5 \times 10^{-6}$

determined. All that is now necessary is to substitute the values in the expression

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

when α is found. Now, using the value of α found at different dilutions, the equation of Ostwald can be tested. Table XCI shows some values for acetic acid, and gives an indication of the validity of the Law for this substance.

It is clear that the Law is obeyed by acetic acid only in dilute solution (v large).

273. Validity of the Dilution Law.—Weak electrolytes obey Ostwald's Dilution Law fairly well, but in the case of strong electrolytes the Law fails completely. This "anomaly" of strong electrolytes has given rise to much interesting speculation on the nature of such solutions. The Table below, based on the work of Kohlrausch and Maltby, gives some figures for the ionisation of potassium chloride, which is a strong electrolyte.

TABLE XCII.—APPARENT DEGREE OF IONISATION OF POTASSIUM CHLORIDE AT 18° C.

$\Lambda_\infty = 129{\cdot}91.$

v.	Λ_v	$\frac{\Lambda_v}{\Lambda_\infty} = \alpha$.	K.
1	98·27	0·7565	2·350
2	102·41	0·7883	1·434
5	107·96	0·8310	0 8154
20	115·75	0·8910	0·3642
50	119·96	0·9234	0·2221
200	124·41	0·9577	0·1084
1,000	127·34	0·9802	0·0485
10,000	129·07	0·9936	0·0154

It will be noted that the values of K are by no means constant.

In order to remove this anomaly, many empirical formulæ have been suggested as dilution laws, very few of them having any theoretical basis. Thus, Walker put forward the equation

$$\frac{\alpha^2}{(1-\alpha)v} = k\,\frac{1-\alpha}{\alpha},$$

or

$$k = \frac{\alpha^3}{(1-\alpha)^2 v}.$$

Van't Hoff put forward the equation

$$\frac{\alpha^{\frac{3}{2}}}{(1-\alpha)v^{\frac{1}{2}}} = k.$$

Possibly the best of all the formulæ for explaining the behaviour of strong electrolytes is

$$\Lambda_\infty - \Lambda_v = kC^{\frac{1}{2}},$$

where C is the concentration, or the reciprocal of v. This equation

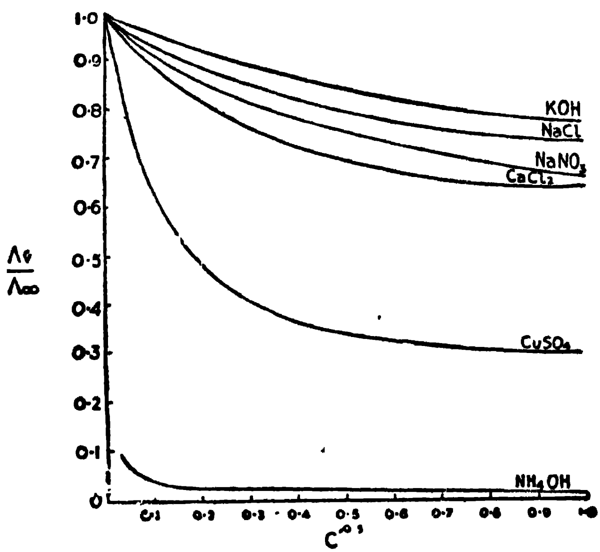


FIG. 181.—Curve between Λ_v/Λ_∞ and $C^{0\cdot5}$.

is ascribed to Kohlrausch, though it appears to have been put forward originally by Bousfield in 1913.

If this equation be true, it is obvious that if $\Lambda_\infty - \Lambda_v$ is plotted against $C^{0\cdot5}$, a straight line should result, passing through the origin. The slope of the line should be k. Or, if Λ_v is plotted against $C^{0\cdot5}$, again a straight line graph should be obtained, but it will not now pass through the origin, but will cut the axis at Λ_∞. It is usual to plot $\dfrac{\Lambda_v}{\Lambda_\infty}$ against the square root of the concentration, and in Fig. 181 are given some curves for various substances. The data upon which the curves are based are given in Table XCIII. It is seen that the equation is only approximately true, holding best for the more dilute solutions. It is, however, very important as a limiting law for very dilute solutions. It may be noted here that the equation

is of the form derived by Debye and Hückel on the basis of the theory of electrostatic interaction (p. 546).

TABLE XCIII.—CONDUCTANCE RATIOS

Substance.	$\frac{\Lambda_v}{\Lambda_\infty}$ for c (gm.-mols. per litre).			
c / $\sqrt{c}$	·001 / ·03162	·01 / ·1	·1 / ·3162	1 / 1
Sodium chloride .	0·977	0·936	0·852	0·741
Sodium nitrate .	0·977	0·932	0·832	0·660
Calcium chloride .	0·954	0·882	0·764	0·662
Copper sulphate .	0·862	0·629	0·396	0·309
Potassium hydroxide .	0·99	0·96	0·90	0·77
Ammonium hydroxide	0·118	0·042	0·014	0·0037

The Kohlrausch equation is found to be approximately true for many aqueous and non-aqueous solutions. Ferguson and Vogel (1927), however, state that the equation is best written in the form

$$\Lambda_\infty - \Lambda_v = Kc^n.$$

n is about 0·5 for many electrolytes, but may vary a good deal from that figure. Thus, for potassium nitrate, it was found to be 0·374, and for iodic acid 0·969.

274. Explanations of the Anomaly of Strong Electrolytes.—The Ostwald Dilution Law was calculated on the basis of two assumptions, *viz.*: (1) that the Law of Mass Action holds for charged ions; and (2) that the Arrhenius hypothesis, that electrolytes are partially dissociated into their ions in aqueous solution, is true, the ratio $\frac{\Lambda_v}{\Lambda_\infty}$ representing the extent of this dissociation.

Since strong electrolytes do not obey the Law, it is clear that one, or both, of these assumptions is not true. There seems to be no reason to doubt the first. The error probably lies in the second. Since the concentrations of the ions are calculated in terms of α, determined by conductivity experiments, it follows that α is not an accurate measure of these concentrations. The conductivity ratio, $\frac{\Lambda_v}{\Lambda_\infty}$, which may now be called f_c, is, therefore, not the degree of dissociation α.

In 1908 Lewis introduced the concept of *activity* to replace the concentration in the Law of Mass Action equation, in order to make the Law accurate (§ 161). This was, at first, merely an empirical

quantity. More recently, however, the concept has been widely used in connection with the work of Debye and Hückel, on the conductivity of electrolytes. Originally used to overcome difficulties in the application of the Law of Mass Action to ordinary homogeneous systems, the concept of activity has been applied to electrochemistry with considerably greater success.

At infinite dilution, the activity of a substance is defined as its concentration. For any other concentration, the activity is not, in general, equal to the concentration. The fraction $\frac{a}{c}$, where a is the activity ("ideal concentration" or active mass) and c the actual concentration, is called the *activity coefficient*, f. Several methods are applicable for the determination of the activity coefficient, but their description is beyond the scope of this book.

Debye and Hückel investigated the fact that the conductivity ratio, $f_c = \frac{\Lambda_v}{\Lambda_\infty}$, does not agree with the degree of dissociation, α, basing their work on the idea that strong electrolytes are completely dissociated, and that there is electrostatic interaction between the ions.

Sutherland (1906) proposed that all strong electrolytes were completely dissociated into their ions at all concentrations, and that the difference in conductivity of a solution at various dilutions was not due to the fact that different numbers of ions were present, but that their mobilities were altered, partly by the change in viscosity in the solution itself, and partly by a kind of electrical viscosity due to interaction between the ions. Little notice was taken of the theory at the time, but it was revived in 1918 by Ghosh, and also received attention at the hands of Milner, Bjerrum, and others.

The best treatment of it, however, has been given by Debye and Hückel (1923) and Onsager. They assume, as has been stated above, that there is complete dissociation for strong electrolytes, and that the mobility of the ions is affected by two kinds of electrical viscosity. Owing to the attraction between positive and negative ions, there will always be an excess of positive ions in the neighbourhood of a negative ion, and *vice versâ*, providing an "ionic atmosphere" round each ion. The situation is very much like that obtaining in the sodium chloride crystal (§ 125), in which one ion is surrounded by eight ions of opposite charge. When the solution is diluted, the ions are separated, and this will require the performance of internal work against the electrostatic attraction, as well as the work due to osmotic pressure. When an electromotive force is applied at electrodes in the solution, suppose the positive ions move

to the right. The "ionic atmosphere" of negative ions has constantly to be renewed to the right of the ion, whilst that on the left dies away. It must be supposed that the formation of the new "ionic atmosphere" on the right does not take place at the same rate as the decay of the old one on the left, but that the latter lags behind. A definite "relaxation time" is required for the right-hand atmosphere to build itself up, whilst the left-hand atmosphere is decaying. There will thus be always a preponderance of negative ions to the left of the positive ion, and they will exert a retarding effect. The electromotive force applied tends to move the ionic atmosphere in a direction opposite to that of the motion of the ion, causing an additional retardation. By taking into account all these effects, which do not seem very concrete when described generally, but which are capable of mathematical treatment, Debye and Hückel showed that both these retardations were proportional to the square root of the concentration. The equation they obtained was

$$1 - f_c = \sqrt{\frac{4\pi e^2}{\epsilon kT}}\left[\frac{e^2}{6\epsilon kT} w_1 + bw_2\right]\sqrt{nc},$$

where e is the charge on a univalent ion, ϵ is the dielectric constant of the solvent, k is Boltzmann's constant (equal to the gas constant R, divided by Avogadro's number, N), T is the absolute temperature, w_1 and w_2 are valency factors, and also depend upon ionic mobilities, and b is the mean ionic diameter. nc represents the ionic concentration, and is obtained by multiplying the molecular concentration c by the number of ions n formed by one molecule. If numerical values are substituted, the solvent being water at 18° C., the equation becomes

$$1 - f_c = [0{\cdot}270 w_1 + 0{\cdot}233 \times 10^8 \times bw_2] \cdot \sqrt{nc}.$$

This agrees with the Kohlrausch equation, which has been given in the form

$$\Lambda_\infty - \Lambda_v = KC^{\frac{1}{2}}.$$

This may be rewritten

$$1 - \frac{\Lambda_v}{\Lambda_\infty} = \frac{K}{\Lambda_\infty} C^{\frac{1}{2}}$$

or

$$1 - f_c = \text{const.}\ \sqrt{c}.$$

This is of the same form as the Debye-Hückel equation. It is seen that the proportionality factor depends upon the valency factors w_1 and w_2 (*i.e.*, upon the charge of the ions), and upon the ionic diameter.

In the case of weak electrolytes, the same retarding forces are at

work, but solutions of this kind are supposed to be incompletely dissociated, and the concentration of the ions would be too small to make the retardation effect of any account.

Whilst the theory that has been used is that of complete dissociation, it is very probable that even in the strongest electrolytes there is not 100 per cent. dissociation. It would be better to say that there is "almost complete dissociation." If it were possible to draw a sharp dividing line between strong and weak electrolytes, it might be argued that the one class was quite different from the other, and that the strong electrolytes were completely dissociated, and the weak electrolytes only partially so. This is not possible, however, for there is a gradation between those electrolytes, commonly classed as weak, which obey Ostwald's Law at medium concentrations, but not at high ones, through the transition electrolytes, which obey the Law at low concentrations, to the strong electrolytes, which do not obey the Law at all. It is impossible to say where one class ends and the other begins; and as we must assume the existence of un-ionised molecules in the solutions of weak electrolytes, and in the transition stage, it seems probable that there is no abrupt change in this capacity to form un-ionised molecules. In strong electrolytes, however, the proportion of these un-ionised molecules must be very much smaller than that given by conductivity measurements $\left(\frac{\Lambda_v}{\Lambda_\infty}\right)$.

The study of the Raman spectra (§ 377) of solutions of acids and salts throws some light on this question. The Raman effect is a molecular light scattering effect; each molecular species gives its own characteristic effect, and hence it is possible to find out whether non-ionised molecules (which would, of course, be a different molecular species from the ions) are actually present in solution. When examined in this way, both nitric and sulphuric acids are found to be only partially ionised in moderately strong and strong solutions. With the Raman effect, it is possible to follow the single-stage ionisation of nitric acid and the two-stage ionisation of sulphuric acid.

With regard to salts, with the exception of the anomalous mercuric chloride and mercuric cyanide, the Raman effect provides no evidence whatever for any undissociated molecules, even in the most concentrated solutions. By undissociated molecules is meant a molecular species in which the ions are bound together by a covalent bond of ordinary chemical strength.

The *X*-ray analysis of crystals of sodium and potassium chlorides, and of many other substances, has shown them to be ionised com-

pletely even in the solid state (§ 125). It would be unlikely for combination of ions to occur when the crystal was dissolved in water, though not impossible.[1] Rubens has shown that the reflection of infra-red rays by these crystals agrees with the assumption that they are completely ionised.

Further evidence can be obtained from consideration of distribution experiments. It has already been stated (§ 216) that distribution of the same molecular species occurs between two immiscible solvents, and if, by some reaction, or alteration in the molecular aggregation, this molecular species is altered, it is only the concentrations of the same molecular species which must be taken into account in calculating the distribution coefficient. Now, silver perchlorate is soluble in benzene, and gives a non-conducting solution. It is therefore un-ionised. If water is shaken up with this benzene solution, the whole of the silver perchlorate is transferred to the aqueous layer. If any un-ionised molecules existed in the aqueous layer, there would be a distribution of them between the benzene and water. Hence, it is concluded that the molecular species formed in the aqueous layer are totally different from those in the benzene layer. Presumably the salt is completely ionised in the aqueous solution.[2] It must be pointed out, however, that many examples are known of the incomplete extraction of strong electrolytes from solutions in non-ionising solvents, and the only explanation of this is that there are un-ionised molecules of the electrolyte in the aqueous solution.

Evidence from vapour pressure observations depends upon the same application of distribution. Hydrogen chloride in aqueous solution has a very low vapour pressure of hydrogen chloride gas. According to Henry's Law (§ 189), the ratio of concentrations of the same molecular species between the gaseous and liquid phases is constant. The fact that the vapour pressure of the gas over the solution is so small was used as an argument for the theory of complete dissociation. The vapour pressure was much less than that required if the Arrhenius hypothesis were correct. But the fact that there is any vapour pressure of the gas at all over the solution indicates that there must, at least, be a very small concentration of un-ionised hydrogen chloride in the aqueous layer.

The conclusion to be drawn from this work is that although the

[1] It might be possible for the molecule to exist in aqueous solution with the electrovalent linkage between the ions unbroken; the ions would be held together by electrostatic forces, and the molecule, although ionised, would be undissociated.

[2] It is, of course, possible that there might be solvated un-ionised molecules in the water layer, which would count as a separate molecular species from that of the solvated, or unsolvated, molecules in the benzene layer.

Debye-Hückel theory is more near the truth than that of Arrhenius, its assumption that strong electrolytes are *completely* dissociated in solutions of moderate concentration is probably not true. Rather is it likely that a *very small* amount of the solute exists in the undissociated state.

275. Hydrogen Ion Concentration.—The most important ion is the hydrogen ion. Upon the concentration of hydrogen ions in a solution depends its acidic or alkaline properties (§ 290). The hydrogen ion is a powerful catalyst, and the whole course of a reaction may be modified by altering the hydrogen ion concentration in the medium in which the reaction takes place. A knowledge of hydrogen ion concentration is necessary in testing water, soil, and biological fluids, such as the blood.

In dealing with hydrogen ion concentration it is usual to express it in a special way. The p_H of a solution is defined as the logarithm to the base 10 of the reciprocal of the hydrogen ion concentration in gm.-mols. per litre. Thus

$$p_H = -\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]}.$$

If the p_H of a solution is 4,

$$\log_{10}\frac{1}{[H^+]} = -\log_{10}[H^+] = 4,$$

and the hydrogen ion concentration is 10^{-4}, *i.e.*, 0·0001 gm.-mol. per litre.

The student should make himself thoroughly familiar with this method of expressing hydrogen ion concentration. It has been adopted because it is frequently necessary to deal with very minute hydrogen ion concentrations, and these are conveniently expressed in this way.

It may be mentioned here that the hydrogen ion, in aqueous solutions, is invariably solvated, *i.e.*, is attached to one or more molecules of water. It is usually supposed that one molecule of water is attached to each hydrogen ion, and the formula of the ion is, therefore, H_3O^+, sometimes called the "hydroxonium" ion. Wherever the hydrogen ion (in aqueous solutions) is mentioned, the H_3O^+ ion is intended, but in order to simplify the work, the ion will be written H^+.

276. The calculation of Hydrogen Ion Concentrations in Acid Solutions.—An example will be taken at this point of the calculation of the p_H value of a solution, given the dissociation constant of the acid.

Thus, it is required to find the p_H value of a $N/100$ solution of acetic acid. The dissociation constant of the acid is $1{\cdot}8 \times 10^{-5}$.

1 From the simplified form of Ostwald's Dilution Law, we have

$$\alpha = \sqrt{Kv}.$$

We can apply this because α is very small. Now, v is the volume containing 1 gm.-mol. of the acid, expressed in litres, *i.e.*, in this case 100. Thus

$$\begin{aligned}\alpha &= \sqrt{100 \times 1{\cdot}8 \times 10^{-5}} = \sqrt{1{\cdot}8 \times 10^{-3}},\\ &= 4{\cdot}242 \times 10^{-2}.\end{aligned}$$

This value of α is the fraction of a gram-molecule dissociated. Hence, in 1 litre of solution there would be $4{\cdot}242 \times 10^{-4}$ gm.-mols. of hydrogen ions. The molecular concentration is $4{\cdot}242 \times 10^{-4}$, and the $p_H = -\log\,[H^+]$

$$\begin{aligned}&= -\,(\bar{4}{\cdot}6276) = -\,(-\,4 + 0{\cdot}6276),\\ &= -\,(-\,3{\cdot}3724),\\ &= 3{\cdot}3724.\end{aligned}$$

Thus the p_H of the solution is 3·37.

Let us now find the p_H of a $N/1{,}000$ solution of acetic acid.

$$\alpha = \sqrt{Kv}, \text{ as before.}$$

v is now 1,000,

$$\begin{aligned}\therefore \alpha &= \sqrt{1{,}000 \times 1{\cdot}8 \times 10^{-5}},\\ &= \sqrt{1{\cdot}8 \times 10^{-2}},\\ &= 1{\cdot}34 \times 10^{-1}.\end{aligned}$$

In 1 litre of the solution there will be $1{\cdot}34 \times 10^{-4}$ gm.-mols. of hydrogen ions. Hence, molecular concentration $= 1{\cdot}34 \times 10^{-4}$.

$$\begin{aligned}p_H = -\log\,[H] &= -\log\,(1{\cdot}34 \times 10^{-4})\\ &= -\,(\bar{4}{\cdot}1271)\\ &= 3{\cdot}8729.\end{aligned}$$

Hence, $$p_H = 3{\cdot}87.$$

ii. The p_H of an acid solution may be calculated in terms of α, and the dissociation constant K, as follows: Consider the ionic equilibrium in a solution of an acid HA,

$$HA \rightleftharpoons H^+ + A^-.$$

Applying the Law of Mass Action,

$$\frac{[H^+]\,[A^-]}{[HA]} = K.$$

If the degree of dissociation is α, then $[H^+] = \alpha$, $[A^-] = \alpha$, and $[HA] = 1 - \alpha$.

Hence, $$[H^+] = K\frac{1-\alpha}{\alpha}.$$

or, $$p_H = \log_{10}\frac{1}{[H^+]} = \log_{10}\frac{1}{K} + \log_{10}\frac{\alpha}{1-\alpha}.$$

277. Methods of determining Hydrogen Ion Concentration.—There are several methods of determining the hydrogen ion concentration of a solution. The chief are

(1) The conductivity method.
(2) The electromotive force method.
(3) The freezing point method.
(4) The colorimetric method.
(5) The method of catalysis of ester hydrolysis.

(1) The conductivity method is simply that of determining the degree of dissociation of the acid. The degree of dissociation, α, is given by

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty},$$

where Λ_∞ and Λ_v are the equivalent conductivities at infinite dilution and at dilution v respectively. These can be determined by the method given in § 272. α is, of course, a direct measure of the hydrogen ion concentration.

(2) [1] The electromotive force method is the most accurate for the determination of hydrogen ion concentration. Use is made of the hydrogen electrode (p. 553), which consists of platinised platinum dipping into the solution of which the p_H is required, through which a current of hydrogen is passed. The platinum catalyses the electrochemical reaction

$$H_2 - 2\epsilon \rightleftharpoons 2H^+.$$

The electrode thus tends to become positively charged when hydrogen ions are converted into gaseous hydrogen, so that the electrode attains a definite potential when the electrostatic force repelling the hydrogen ions stops further discharge. The potential depends upon the concentration of hydrogen ions and the concentration of hydrogen gas.

To derive the relationship between hydrogen ion concentration and the e.m.f. of the hydrogen electrode, we may consider a concentration cell (p. 642), consisting of two electrodes of the same metal placed in solutions of concentration C_1 and C_2 separated by a porous partition. The solutions are of a salt of the electrode metal. The potential of a metal with respect to a solution of one of its salts is dependent on the concentration of the salt. Let the valency of the cation be n, and the potentials of the electrodes with respect to the

$$\begin{array}{ccccccc} M & | & M^+ & \vdots & M^+ & | & M \\ & E_1 & C_1 & e & C_2 & E_2 & \end{array}$$

e is neglected.

[1] This section will be more clearly understood after reading § 322, and may be postponed until then.

solution be E_1 and E_2. Suppose 1 gm.-atom of metal is dissolved off the one electrode, and deposited on the other. Then, an amount of electricity nF coulombs, where F is the Faraday, has passed round the circuit. The electrical work done is $nF(E_1 - E_2)$, assuming that there is no potential at the partition.

This same process of transferring a gram-atom of metal from one concentration to another can be done by an isothermal and reversible expansion, doing work against the osmotic pressure. Supposing that the ions obey the gas laws, and p is the osmotic pressure exerted by them, the work done is $\int_{v_1}^{v_2} pdv$, where v_1 and v_2 are the reciprocals of C_1 and C_2 respectively.

$$\int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} \frac{RT}{v}\, dv = RT \log_e \frac{v_2}{v_1} = RT \log_e \frac{C_1}{C_2}.$$

Now, it is obvious that if there are two ways in which a change can be made in a system isothermally and reversibly, the work done in both cases must be the same. We therefore equate the two amounts of work :—

$$nF(E_1 - E_2) = RT \log_e \frac{C_1}{C_2}, \text{ or } E_1 - E_2 = \frac{RT}{nF} \log_e \frac{C_1}{C_2}$$

$$= \frac{2{\cdot}303RT}{nF} \log_{10} \frac{C_1}{C_2}.$$

Substituting the value of R ($8{\cdot}315 \times 10^7$ ergs), and F (9,650 c.g.s.), the value of $\frac{2{\cdot}303RT}{F}$ can be calculated. At 15° C. it comes to 0·058. Hence, the simplified formula

$$E_1 - E_2 = \frac{0{\cdot}058}{n} \log_{10} \frac{C_1}{C_2}$$

is used.

It is obvious from this equation that if we know $E_1 - E_2$, n, and C_1 we can find C_2.

Hydrogen gas, in contact with a solution containing hydrogen ions, acts like a metal in contact with a solution containing ions of the metal. The potential of the hydrogen electrode in a solution normal with respect to hydrogen ions is taken as zero, and all other electrode potentials are measured from this. Thus, if we put $n = 1$, $E_2 = 0$, $C_2 = 1$, the e.m.f. of the theoretical electrode mentioned in the above proof is

$$E_1 = 0{\cdot}058 \log_{10} C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Thus, if we had two hydrogen electrodes, one placed in a solution normal with respect to hydrogen ions and the other in a solution of

which the hydrogen ion concentration was required, the two solutions being separated by a porous partition or a bridge of some kind, by measuring the difference of potential we should find the hydrogen ion concentration by using the equation (1) above.

The hydrogen electrode used in practice may take one of many forms. The essentials are, however, shown in the left-hand electrode of Fig. 182. Hydrogen under a known pressure bubbles through a solution containing hydrogen ions, in which is immersed a strip of platinised platinum foil. Electrical connection is made with this foil.

However, it is not always easy to get exact normality, and it is difficult to set up such an electrode, so one hydrogen electrode is usually replaced by a *calomel electrode*, which has a constant

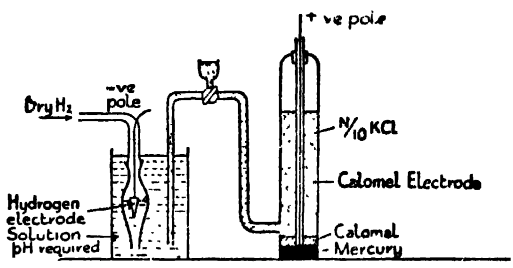


FIG. 182.—Arrangement of Cell for determining Hydrogen Ion Concentration.

potential, known on the hydrogen scale. The calomel electrode is really a mercury concentration electrode. It is made by placing a pool of mercury at the bottom of a vessel, and covering it with a paste of pure mercurous chloride, mercury and potassium chloride solution. The strength of the latter partly determines the e.m.f. of the electrode; hence, the strength must be specified. It is usual to employ $N/10$, N, or saturated solution. The cell is filled with potassium chloride solution of the correct strength, saturated with mercurous chloride.

A diagram of the two electrodes, arranged to determine the hydrogen ion concentration of a solution, is given above. The determination of the e.m.f. of the cell, by means of a potentiometer, calls for no description, as it is given in the practical text-books.

The e.m.f. of the calomel electrode referred to the normal hydrogen electrode is 0·3989 volts.

The quinhydrone electrode is another arrangement in use for determination of electrode potentials. It is not of such general use

as the hydrogen electrode, since it can only be used for acid solutions in which the p_H is numerically less than 7, and is not reliable in the presence of certain neutral salts. It is, however, easier to set up than the hydrogen electrode, and does not require a continuous supply of hydrogen.

If quinone and its reduction product, hydroquinone, are present together in a solution which also contains hydrogen ions, the following reversible reaction can take place

$$\underset{\text{Quinone.}}{C_6H_4O_2} + 2H^+ \rightleftharpoons \underset{\text{Hydroquinone.}}{C_6H_6O_2} - 2\epsilon$$

provided that the electricity 2ϵ is removed. This can readily be done by placing in the solution a piece of platinum foil and making the arrangement part of a cell. The potential of the electrode can be obtained by a method similar to the last. By direct comparison of a quinhydrone electrode against a hydrogen electrode, the expression

$$E = 0{\cdot}704 + 0{\cdot}058 \log_{10} [H^+]$$

was found by Biilmann to give the e.m.f. of the electrode at 18° C.

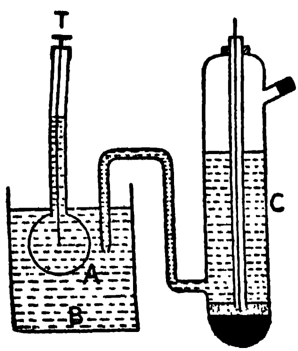


FIG. 183.—Glass Electrode.

The Glass Electrode.—When a glass surface is in contact with a solution, it acquires a potential, which depends upon the hydrogen ion concentration of the solution. This observation, which was made as far back as 1909 by Haber and Klemensiewicz, is now used as a basis of a method of determining the p_H of a solution where other electrodes cannot be used. The glass electrode consists essentially of a very thin-walled glass bulb, A, made of a low melting point glass, blown at the end of a glass tube. This is filled with an electrolyte, *e.g.*, *N* hydrochloric acid saturated with quinhydrone. The upper end of the tube is ground, and a terminal, T, bearing a platinum wire, with which electrical contact is made with the electrolyte in the tube, is fitted over the ground portion. The bulb is then placed in the liquid B, of which the p_H is required and the potential is measured against a standard electrode C by means of a potentiometer. Since the resistance is high, a special galvanometer must be used. The potential of the electrode is connected with the p_H of the solution by the equation

$$E_g = K + \frac{RT}{F} \log_e [H^+].$$

K is a constant for the electrode depending upon the nature of the glass and the electrolyte used in the bulb. It can be determined by finding the e.m.f. produced in buffer solutions of known p_H. If a curve is drawn between p_H and e.m.f., the p_H of any solution measured with the glass electrode can then be read off directly when the e.m.f. produced is known.

The nature of the glass used is of importance. It must not be appreciably attacked by the liquid under test, and yet must have as high a conductivity as possible. The latter condition is fulfilled by soda-glass, but this is very easily attacked. For this reason, the results obtained by the glass electrode are not reliable for alkaline solutions of p_H greater than 10.

By the electromotive force method accurate determinations of p_H can be made, and if the apparatus is kept ready, as it can be, where the determination has frequently to be made, it is quite rapid. Under ordinary circumstances, however, it would be too slow.

(3) The freezing point method is only another way of determining the degree of dissociation, from which, of course, the p_H can be obtained. Knowing the true molecular weight of the acid, the molecular depression of the solvent used, and the depression of the freezing point caused by the solution of a known weight of acid in a given weight of solvent, α can be determined as previously indicated (§ 256). $PV = iRT$; $i = (n-1)\alpha + 1$.

(4) The colorimetric method. This depends on the use of indicators (§ 286). Only a brief indication of the application of the method will be given. Indicators are known which change their colour at various values of p_H, and, indeed, there is a universal indicator, a mixture of several indicators, which changes colour from purple, through blue, green, yellow, orange to red as the p_H changes in the direction of greater acidity. A series of buffer solutions is prepared (§ 284). A drop of the universal indicator is added to each of these, thus colouring each differently. The solution of unknown p_H is taken, a drop of the indicator is added, and the colour compared with that of the standards. In this way the tube matching with the unknown solution gives the p_H.

This is the simplest, and most satisfactory, method where speed combined with moderate accuracy is required. There are indicator methods which do not involve the use of buffer solutions, but these do not yield such accurate results and are not so convenient.

(5) The method using the catalysis of ester hydrolysis will be discussed in connection with the determination of the strengths of acids (§ 293).

278. The Ionisation of Water.—When hydroxyl ions and hydrogen ions are brought together, water is formed, which is practically

undissociated. Water is very nearly an insulator, but the fact that the purest water will conduct the current a little points to the fact that it must be slightly broken down to its ions. The union of hydroxyl and hydrogen ions to form water is neatly shown by the ionic explanation of the fact that the heat of neutralisation of a strong acid by a strong base is always in the neighbourhood of 13,700 gm.-cals per gm.-mol. (§ 306). Thus, if hydrochloric acid and sodium hydroxide, in equivalent proportions in dilute solution, are mixed, there is an evolution of heat to the extent of 13,700 gm.-cals. per gm.-mol. The same is true for hydrochloric acid, and potassium hydroxide, and of nitric acid and a strong base. The following Table shows the heat of neutralisation of some of the commoner acids with sodium hydroxide.

TABLE XCIV.

Acid.	Heat of Neutralisation.
	Gm.-cals. per gm.-mol.
Hydrochloric	13,700
Nitric	13,700
Hydriodic	13,700
Hydrobromic	13,800
Chloric	13,800
Acetic	13,400
0·5 gm.-mol. Sulphuric	15,700
Hydrofluoric	16,300

The fact that the heat of neutralisation per gm.-mol. of all these acids is about the same indicates that there must be a common reaction taking place for them all. If the ionic equation for an acid, say HA, reacting with sodium hydroxide is written, we have

$$H^+ + A^- + Na^+ + OH^- \rightleftharpoons H_2O + Na^+ + A^-,$$

since the salt formed will be well ionised. Thus, the net reaction is merely the union of hydrogen and hydroxyl ions to form the comparatively little dissociated water. This is the same with all strong acids and bases, particularly if the neutralisation is carried out in dilute solution, for then the dissociation of the reactants is complete.

The ionisation of water is a reversible process. Hence, the Law of Mass Action will apply to it. Although water is but little ionised, this ionic equilibrium is one of the most important in physical chemistry, for it will explain many properties of aqueous solutions of electrolytes.

It is therefore of some interest to discover to what extent water is ionised. The usual method of finding the degree of dissociation is, of course, to determine the conductivity and calculate α from the result. Water conducts very feebly, and the presence of impurities makes a tremendous difference to the value obtained for the conductivity.

Kohlrausch and Heydweiller determined the specific conductivity of the purest distilled water (p. 515) and found it to be $0{\cdot}0384 \times 10^{-6}$ mhos at 18° C. We obviously cannot determine directly the equivalent conductivity at infinite dilution, but we can derive the corresponding figure by adding the ionic conductances at infinite dilution of the hydrogen and hydroxyl ions (§ 259). The value for hydrogen is 313, and for hydroxyl 174 mhos. Hence, the equivalent conductivity of completely ionised water will be 487 mhos. The equivalent conductivity is equal to the specific conductivity multiplied by the volume in c.c. containing one gram-equivalent of the ions. Hence, the volume containing one gram-equivalent of hydrogen and hydroxyl ions

$$= \frac{487}{0{\cdot}0384 \times 10^{-6}} \text{ c.c.,}$$
$$= 1{\cdot}27 \times 10^{10} \text{ c.c.}$$

Hence, the hydrogen ion concentration is

$$\frac{1}{1{\cdot}27 \times 10^{10}} \text{ gm.-equivs. per c.c.}$$
$$= 0{\cdot}78 \times 10^{-10} \text{ gm.-equivs. per c.c.}$$
$$= 0{\cdot}78 \times 10^{-7} \text{ gm.-equivs. per litre.}$$

As stated above, the ionisation of water is a reversible process, and the Law of Mass Action can be applied to it. In the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

the amount of undissociated water is so great that its concentration may be regarded as constant. Hence,

$$[H^+]\,[OH^-] = K_w.$$

K_w is the ionic product for water. Taking the figures derived above,

$$K_w = 0{\cdot}78 \times 0{\cdot}78 \times 10^{-14} = 0{\cdot}61 \times 10^{-14}.$$

This is the value at 18° C. The conductivity of pure water increases rapidly with the temperature, and the following Table shows the values of K_w at various temperatures.

T° C. .	0	18	25	50	75	100	128	136	218
$K_w \times 10^{14}$	0·09	0·61	1·0	4·5	16·9	48	114	220	461

The value at 25° C. is usually taken as standard, because it is a

convenient temperature for working and happens to give the value unity for the ionic product ($\times\ 10^{14}$).

It is to be noted that K_w is the ionic product, and not the dissociation constant of the reaction. The value of the latter at 18° C. would be given by

$$\frac{[H^+][OH^-]}{[H_2O]} = \frac{(0{\cdot}78 \times 10^{-7})^2}{\left(\frac{1{,}000}{18}\right)} = \frac{1}{55}\left(0{\cdot}78 \times 10^{-7}\right)^2.$$

Another method of determining the concentrations of hydrogen and hydroxyl ions in water is that due to Wijs, who determined the rate of hydrolysis of methyl acetate in pure water.

$$CH_3.COOCH_3 + H^+ + OH^- \rightleftharpoons CH_3.OH + CH_3.COO^- + H^+.$$

It is clear that in this reaction, as it proceeds towards the right, the concentration of hydrogen ions increases, relative to that of the hydroxyl ions. It was shown that hydroxyl ions were much more effective catalysts for this hydrolysis than the hydrogen ions, being, in fact, about 1,400 times as active. The reaction velocity would therefore reach a minimum when the hydrogen ion concentration was 1,400 times as great as that of hydroxyl ions. From his results Wijs calculated that K_w was $1{\cdot}44 \times 10^{-14}$, at 25° C.

The value of the ionic product has been obtained by several other methods, and a list of the values derived is given in the accompanying Table :—

Table XCV.

Method.	K_w at 25° C.
Conductivity of pure water . . .	$1{\cdot}0 \times 10^{-14}$
Hydrolysis of sodium acetate . . .	$1{\cdot}15 \times 10^{-14}$
Hydrolysis of methyl acetate . . .	$1{\cdot}44 \times 10^{-14}$
E.m.f. of hydrogen-oxygen cell . . .	$1{\cdot}01 \times 10^{-14}$

There is thus little doubt of the order of this dissociation, and, for all ordinary purposes, the value of K_w is taken as 10^{-14} at 25° C.

Knowing the value of the ionic product, which is a multiple of the dissociation constant, at two different temperatures, we can calculate the heat of ionisation (Q) of water by making use of van't Hoff's equation (§ 321). This states

$$\log_{10} K_1 - \log_{10} K_2 = \frac{-Q}{4{\cdot}576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Now, for $T_1 = 0° C. = 273° Abs., K_1 = 0{\cdot}09 \times 10^{-14}$
$T_2 = 50° C. = 323° Abs., K_2 = 4{\cdot}5 \times 10^{-14}$

$$\log (0{\cdot}09 \times 10^{-14}) - \log (4{\cdot}5 \times 10^{-14}) = \frac{-Q}{4{\cdot}576}\left(\frac{1}{273} - \frac{1}{323}\right)$$

$$-1{\cdot}6990 = \frac{-Q}{4{\cdot}576}\left(\frac{50}{88{,}180}\right)$$

$$\therefore Q = \frac{4{\cdot}576 \times 1{\cdot}6990 \times 8818}{5}$$

$$= 13{,}720 \text{ gm.-cals. per gm.-mol.}$$

Now Q, the heat of ionisation, should be the amount of heat given out when a strong base neutralises a strong acid in dilute solution if the theory is correct. It is seen that there is very good agreement between the calculated and observed values, which provides good evidence for the accuracy of the theories involved.

279. Hydrolysis of Salts.—Nearly every salt when dissolved in water exhibits a slight acid or alkaline reaction; the solution is hardly ever perfectly neutral. This is due to the action of water on the salt, and the phenomenon is known as *hydrolysis*. It is ultimately caused by the fact that the acid and the base which have combined to make the salt have not been of exactly the same strength. If the strengths are exactly the same, a truly neutral solution is obtained when the salt is dissolved in water. Take, for example, sodium chloride, NaCl. This is made by the combination of a strong acid and a strong base, and hence the resultant salt is neutral. Ferric chloride, on the other hand, exhibits an acid reaction in aqueous solution. This is because it is made by the combination of a strong acid, HCl, and a weak base, $Fe(OH)_3$. Sodium borate is alkaline in solution, since it is a compound of a strong base, sodium hydroxide, and a weak acid, boric. The cause of the acid or alkaline reaction is entirely due to the presence of water, and ultimately to the ions of water, and it is for this reason that the process is called hydrolysis.

280. Qualitative Demonstration of Hydrolysis.—(1) Indicators, if they are sufficiently sensitive, when added to solutions will show, by their colour changes, that hydrolysis has taken place.

(2) In the case of some substances, special features may be made use of to indicate the presence of hydrolysis. Thus, ferric chloride will give a solution which on dialysis separates into a solution containing colloidal ferric hydroxide, and another which is strongly acid.

Solutions of ammonium salts will sometimes smell of ammonia when the hydrolysis is pronounced, owing to the greater volatility

of ammonia than of acid. Similarly, potassium cyanide solution smells of hydrocyanic acid.

281. Quantitative Treatment of Hydrolysis.—What actually happens when a salt like ferric chloride hydrolyses? The fact that hydrolysis takes place is primarily due to the dissociation of water into its ions,

$$H_2O \rightleftharpoons H^+ + OH^-.$$

Ferric chloride ionises as follows :—

$$FeCl_3 \rightleftharpoons Fe^{+++} + 3Cl^-.$$

The ferric ions find themselves in the presence of hydroxyl ions, with which they will partially combine to form ferric hydroxide which is only very slightly ionised and very slightly soluble, and is therefore thrown out of solution (as a colloid).

$$Fe^{+++} + 3OH^- \rightleftharpoons Fe(OH)_3.$$

This removes hydroxyl ions from the sphere of action, and the ionic equilibrium of the water is disturbed. The ionic product $[H^+][OH^-]$ must, if the Law of Mass Action be true, remain constant. Hence, more water will ionise, and the hydrogen ion concentration will now be in excess. A solution containing an excess of hydrogen ions is acidic. Hence, a solution of ferric chloride in water will be acid in reaction. Summing up, the reaction is

$$Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+.$$

Taking as another example the case of sodium carbonate, we find that here again the ionisation of water is the key to the whole situation. The sodium carbonate ionises as follows :—

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}.$$

Now the carbonate radical will combine with hydrogen ions to give the feebly dissociated carbonic acid (feebly dissociated because it is a weak acid). This process removes hydrogen ions from the sphere of action, and more water ionises to keep the ionic product constant. But the solution now contains an excess of hydroxyl ions, which is only the same thing as saying that it is alkaline.

In the case of sodium chloride, the salt of a strong acid and a strong base, the ionisation takes the following course :—

$$NaCl \rightleftharpoons Na^+ + Cl^-.$$

If the sodium ions were to combine with the hydroxyl ions of the water they would form sodium hydroxide, which is very nearly completely dissociated, so the hydroxyl ion concentration does not change. Similarly, if the chlorine ions were to combine with the hydrogen ions of the water, they would only form the strong acid, hydrochloric, which is fully ionised, and so there would be no change in the hydrogen ion concentration. The solution therefore contains

as many hydroxyl as hydrogen ions, just as neutral water does, and therefore the solution is neutral.

Degree of Hydrolysis.—The strength of an acid or a base is measured by its dissociation constant (§§ 271, 293), so the extent of hydrolysis taking place will also depend upon this.

The degree of hydrolysis, *h*, is defined as the fraction of the total salt hydrolysed. Thus, if in a solution of aniline hydrochloride, $C_6H_5NH_2HCl$, 95 per cent. of the salt is hydrolysed into aniline and hydrochloric acid, the degree of hydrolysis, *h*, is 0·95, or may be expressed as a percentage, 95 per cent.

The degree of hydrolysis can be calculated from the ionisation constants of the substances involved in the following way :—

I. The general reaction for the hydrolysis of the *salt* (BA) *of a strong base and a weak acid* is

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA,$$

or

$$A^- + H_2O \rightleftharpoons OH^- + HA.$$

Now $[A^-]$ is proportional to the concentration of unhydrolysed salt,
$[OH^-]$ is proportional to the concentration of free base,
and $[HA]$ is proportional to the concentration of free acid.

$$\therefore \frac{k'[OH^-]\,k''[HA]}{k'''[A^-]} = \frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrolysed salt}]} = K_h \quad . \quad . \quad . \quad (1)$$

the concentration of water being regarded as constant. K_h is called the *hydrolysis constant*, and it must be borne carefully in mind that it is not the degree of hydrolysis, although the latter can be obtained from it by calculation.

Now let
$$[H^+][OH^-] = K_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
and
$$\frac{[H^+][A^-]}{[HA]} = K_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_w is the ionic product for water, and K_a is the dissociation constant of the acid.

Dividing (2) by (3), we have

$$\frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} = K_h.$$

Thus the hydrolysis constant, K_h, is the ratio of the ionic product for water to the dissociation constant, K_a, of the weak acid.

II. The equation in the case of the *salt* (BA) *of a strong acid and a weak base* is derived in a similar way. In this case the general equation is

$$B^+ + A^- + H_2O \rightleftharpoons H^+ + A^- + BOH,$$

or

$$B^+ + H_2O \rightleftharpoons BOH + H^+.$$

Applying the Law of Mass Action, we have

$$\frac{[BOH][H^+]}{[B^+]} = K_h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the concentration of water being regarded as constant. Now $[H^+]$ is proportional to the concentration of the free acid, $[BOH]$ to that of free base, and $[B^+]$ to that of unhydrolysed salt. The equilibria involved are

$$H^+ + OH^- \rightleftharpoons H_2O,\ K_w = [H^+][OH^-] \quad . \quad . \quad . \quad . \quad (6)$$

and
$$\frac{[B^+][OH^-]}{[BOH]} = K_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Dividing (6) by (7), we get

$$\frac{[BOH][H^+]}{[B^+]} = K_h = \frac{K_w}{K_b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus, in the case of the salt of a weak base and a strong acid, the hydrolysis constant is the ratio of the ionic product for water to the dissociation constant of the weak base.

A very similar method of treatment leads to the relationship for the case of a *salt of a weak acid and a weak base.* Take, for example, aniline acetate. This hydrolyses as follows :—

$$C_6H_5.NH_2.CH_3.COOH + HOH \rightleftharpoons \underset{\text{Hypothetical anilinium hydroxide.}}{C_6H_5.NH_3OH} + CH_3.COOH.$$

If we assume that the salt is completely ionised, we have

$$C_6H_5NH_3^+ + CH_3.COO^- + H.OH \rightleftharpoons C_6H_5.NH_3.OH + CH_3.COOH;$$

or, in general,

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA.$$

$$\therefore \frac{[BOH][HA]}{[B^+][A^-]} = K_h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The equilibria involved are :—

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$K_b = \frac{[OH^-]\ [B^+]}{[BOH]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$K_w = [H^+][OH^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\therefore \frac{K_w}{K_a.K_b} = \frac{[H^+][OH^-][HA][BOH]}{[H^+][A^-][OH^-][B^+]} = \frac{[HA][BOH]}{[B^+][A^-]} = K_h.$$

We can sum up these results as follows :—

For the salt of a *weak acid*, and a *strong base*, $K_h = \dfrac{K_w}{K_a}$.

For the salt of a *weak base* and a *strong acid*, $K_h = \dfrac{K_w}{K_b}$.

For the salt of a *weak acid* and a *weak base*, $K_h = \dfrac{K_w}{K_aK_b}$.

Notice that it is always the dissociation constant of the weak constituent that appears in the denominator.

These formulæ can only be regarded as approximately true, for they have been derived on the basis of assumptions which are probably in part inaccurate.

The relationship between K_h and h follows from consideration of equation (1), p. 561. We have for the equation for the hydrolysis of a salt of a strong base and a weak acid

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA,$$

or

$$A^- + H_2O \rightleftharpoons OH^- + HA.$$

If one gram-molecule of the salt is dissolved in v litres of water, and h is the degree of hydrolysis, the molecular concentration of unhydrolysed salt is $\frac{1-h}{v}$, and that of the hydrolysed salt and of the free acid will be $\frac{h}{v}$.

Hence, $$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{h^2}{v(1-h)}.$$

If h is small, $vK_h = h^2$.

As an example of the use of the above equations, we will calculate the degree of hydrolysis of $N/10$ and $N/100$ solutions of potassium cyanide. The dissociation constant of hydrogen cyanide is $7 \cdot 2 \times 10^{-10}$ at 25° C.

Potassium cyanide is the salt of a strong base and a weak acid,

$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{7 \cdot 2 \times 10^{-10}}$$
$$= 1 \cdot 389 \times 10^{-5}.$$

Now, the reaction is

$$K^+ + CN^- + H_2O = K^+ + OH^- + HCN,$$

or

$$CN^- + H_2O = OH^- + HCN$$

and $$K_h = \frac{[OH^-][HCN]}{[CN^-]}.$$

The degree of hydrolysis is h. In $N/10$ solution $[OH^-] = \frac{h}{10} = [HCN]$ and $[CN^-]$ $\frac{1-h}{10}$.

$$\therefore \frac{\frac{h^2}{100}}{\frac{1-h}{10}} = K_h = 1 \cdot 389 \times 10$$

$$\frac{h^2}{1-h} = 1 \cdot 389 \times 10^{-4}$$

h will be small and can be neglected with respect to 1.

$$\therefore h^2 = 1\cdot39 \times 10^{-4}$$
$$h = 1\cdot18 \times 10^{-2}.$$

In $N/100$ solution, $[OH] = \frac{h}{100} = [HCN]$, and $[CN^-] = \frac{1-h}{100}$.

$$\therefore \frac{\frac{h^2}{10,000}}{\frac{1-h}{100}} = 1\cdot389 \times 10^{-5}$$

$$\frac{h^2}{1-h} = 1\cdot389 \times 10^{-3}.$$

Neglecting h with respect to 1, we have

$$h^2 = 1\cdot39 \times 10^{-3}$$
$$\therefore h = 3\cdot77 \times 10^{-2}.$$

282. Determination of the Degree of Hydrolysis of a Salt.—There are several methods of doing this, including the following :—

(1) The Distribution Method.
(2) The Conductivity Method.
(3) The Colligative Property Method.
(4) The Catalysis Method.
(5) The Electromotive Force Method.
(6) The use of Indicators.

(1) *The Distribution Method.*—It is obvious that the ordinary methods of chemical analysis cannot be used to investigate the equilibrium, for this would be shifted by their application. A physical method must therefore be used. In the distribution method, a solvent is taken which will dissolve one of the products of the hydrolysis. The distribution of this substance between the solvent and water is first determined, so that the concentration of the substance in the solvent, if subsequently determined, is an index of the concentration in the aqueous layer.

The degree of hydrolysis of aniline hydrochloride may be found in this way. First it is necessary to determine the distribution coefficient of aniline between water and benzene. This is done by shaking 10 gms. of aniline with 1,000 c.c. of water, and 60 c.c. benzene. Withdraw 50 c.c. from the benzene layer, and determine the amount of aniline in it by passing in dry hydrogen chloride gas. This precipitates the aniline as hydrochloride, in which form it may be weighed by evaporating off the excess of benzene on the water bath. From the weight of the hydrochloride, the weight of aniline in the benzene layer can be found. The rest must be in the water layer. Taking the volume of the benzene layer as 59 c.c., allowing

1 c.c. for solution in water, the concentrations of aniline in the two layers are found, and the distribution coefficient determined.

Now take 10 gms. of aniline hydrochloride (or the equivalent of aniline and hydrochloric acid) and shake up as before with 60 c.c. benzene and 1,000 c.c. water. Determine the amount of aniline in the benzene layer by precipitation with dry hydrogen chloride. From the distribution coefficient we know the weight of free aniline in the aqueous layer, and from this the degree of hydrolysis can be found.

Let D be the distribution coefficient of the aniline between benzene and water, and v the volume of benzene, in litres, taken to 1,000 c.c. water.

Let c_1 be the concentration of base in the aqueous layer, in gram-equivalents per litre, and c_2 the original concentration of the salt in gram-equivalents per litre.

As there is c_1 of base in the aqueous layer, there must also be c_1vD in the benzene layer, so that the total concentration of the base is $c_1(1 + vD)$. Hence, concentration of the unhydrolysed salt is $c_2 - c_1(1 + vD)$. There must also be, in the aqueous layer, acid of concentration $c_1(1 + vD)$.

Applying the Law of Mass Action to the equilibrium

$$\text{salt} + \text{water} \rightleftharpoons \text{base} + \text{acid},$$

$$\frac{[\text{base}]\,[\text{acid}]}{[\text{salt}]} = K_h.$$

Substituting the values found, we have

$$\frac{c_1^2(1 + vD)}{c_2 - c_1(1 + vD)} = K_h,$$

from which K_h can be readily calculated. The degree of hydrolysis can be calculated from this.

(2) *The Conductivity Method.*—When hydrolysis takes place, hydrogen or hydroxyl ions are formed, and as these have a very high mobility, the conductivity of the solution is increased considerably by hydrolysis.

Taking the case of the salt of a strong base and a weak acid, we have

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA,$$

or

$$A^- + H_2O \rightleftharpoons OH^- + HA.$$

The solution now contains free A^- ions and free OH^- ions, and the solution will owe its conductivity mainly to the OH^- ions. The equation for the equilibrium derived from the Law of Mass Action is

$$\frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrolysed salt}]} = K_h.$$

If we now add a little of the free acid, which, being weak, may be taken as practically non-ionised, we increase [free acid], and hence increase [unhydrolysed salt], in order to keep the value of K_h constant. In other words, the hydrolysis is repressed without altering, to any great extent, the number of OH^- ions present. It is possible, by finding the conductivity of solutions of the pure salt, and of solutions containing excess of the weak acid, or the weak base, to arrive at the degree of hydrolysis of the salt.

Consider the above equilibrium

$$\text{salt} + \text{water} \rightleftharpoons \text{base} + \text{acid}.$$

Suppose we have one gram-equivalent of salt originally present in v c.c., and h is the degree of hydrolysis. The concentrations of the unhydrolysed salt, the base and the acid will be $\frac{1-h}{v}$, $\frac{h}{v}$ and $\frac{h}{v}$ respectively. For the equivalent conductivity of the solution at this dilution, we have

$$\Lambda_v = (1-h)\Lambda'_v + h\Lambda''_v,$$

where Λ'_v and Λ''_v are the equivalent conductivities of the unhydrolysed salt and of the strong base respectively. The acid, being weak, is supposed to be un-ionised and consequently does not add to the conductivity. Hence,

$$h = \frac{\Lambda_v - \Lambda'_v}{\Lambda''_v - \Lambda'_v}.$$

We can determine Λ_v, and Λ'_v can be obtained by measuring the conductivity in the presence of the weak acid which wholly represses the hydrolysis, and does not itself add to the conductivity. Λ''_v can be determined separately, and thus h can be found.

(3) *The Colligative Property Method.*—In the equation

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$

there is obviously an increase in the number of individuals present, water not being counted. This will result in a lowering of the vapour pressure, and hence a lowering of freezing point and elevation of boiling point. By determining the effect of the hydrolysis on one of these we can find the degree of hydrolysis. Since these methods are not very sensitive, it is clear that they can only be used with accuracy for substances that are highly hydrolysed.

(4) *The Catalysis Method.*—This is very similar to the method for determining the hydrogen ion concentration of a solution (§ 293). Hydrogen ions and hydroxyl ions are able to catalyse certain reactions, *e.g.*, the hydrolysis of an ester. By determining the speed of the catalysed reactions the concentration of the catalysing ion can be found. This is hardly an example of true catalysis, as the effect is proportional to the concentration of the ion.

(5) *The Electromotive Force Method.*—This, again, is merely a method of determining hydrogen ion concentration, and hence will not be described in full here. Reference should be made to § 277. A cell is made of a hydrogen electrode and a suitable reference electrode (say calomel), and its e.m.f. determined by means of a potentiometer. The difference of potential observed is made up of two parts : (1) that between the normal hydrogen electrode and the hydrogen ions in the solution ; and (2) that between the reference electrode and the hydrogen ions. The formula, as derived in § 277, is

$$E_1 - E_2 = \frac{RT}{nF} \log \frac{C_1}{C_2}$$

from which the p_H and hence the degree of hydrolysis can be determined.

(6) *The Indicator Method.*—This is just the same as the indicator method of determining hydrogen ion concentrations (§ 277). It only gives an accurate estimate of the hydrolysis where this is not too great.

As an example, suppose that a solution containing x gram-molecules of the salt of a strong acid and a weak base, dissolved in 1 litre of water, is investigated. The p_H of this solution is found to be 5·8, say. It is required to find the degree of hydrolysis. The equation governing the hydrolysis is

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

If h is the degree of hydrolysis, the amount of B^+ left will be $x(1 - h)$, and the amounts of BOH and H^+ formed will be xh. The concentration of hydrogen ions may be found from the p_H value as follows :—

$$\begin{aligned} -\log_{10} [H^+] &= 5{\cdot}8, \\ \log_{10} [H^+] &= \bar{6}{\cdot}2000 \\ [H^+] &= 1{\cdot}585 \times 10^{-6} \text{ gm.-mols. per litre.} \end{aligned}$$

Hence $xh = 1{\cdot}585 \times 10^{-6}$ gm.-mols. per litre. Knowing x, h can be calculated.

283. Determination of the Ionic Product for Water from Consideration of Hydrolysis.—For the hydrolysis of the salt of a weak acid and a strong base the value of the hydrolysis constant, K_h, is given by

$$K_h = \frac{K_w}{K_a}.$$

If we can find K_h and K_a we can obviously find K_w, provided that the method used for finding K_h does not involve the use of K_w.

As an example, we can take the hydrolysis of sodium acetate. For a $M/10$ solution at 25° C., the hydrolysis amounts to 0·008 per cent.

$$\therefore \text{[acid]} = \text{[base]} = 0{\cdot}00008 \times 0{\cdot}1$$

$$\text{[salt]} = 0{\cdot}1 \text{ (neglecting the very small amount hydrolysed)}$$

$$\therefore K_h = \frac{\text{[acid] [base]}}{\text{[unhyd. salt]}} = \frac{(0{\cdot}000008)^2}{0{\cdot}1} = 0{\cdot}64 \times 10^{-9}.$$

Now K_a for acetic acid $= 1{\cdot}8 \times 10^{-5}$.

$$\therefore K_w = K_a K_h = 1{\cdot}8 \times 10^{-5} \times 0{\cdot}64 \times 10^{-9}$$

$$= 1{\cdot}2 \times 10^{-14}$$

i.e., $[H^+]\,[OH^-] = 1{\cdot}2 \times 10^{-14}$,

or $[H^+] = [OH^-] = 1{\cdot}1 \times 10^{-7}$

284. Solutions of Reserve Acidity and Alkalinity.—Even the purest water does not retain a p_H value of 7 for very long. The reason for this is that carbon dioxide in the air dissolves in the water and gives it a slight acid reaction, or silicates may be dissolved from the glass in which the water is kept, and the smallest trace of these impurities gives rise to an alteration in the p_H value. It is sometimes necessary [as will have been seen in the section (§ 277) on the colorimetric method of determining hydrogen ion concentration] to prepare solutions of known p_H value, and to know that this p_H will not alter when, say, a drop of indicator is added to the solution. Such solutions, which are reasonably permanent in p_H value, are called solutions with reserve acidity or alkalinity, or more often *buffer solutions*.

Buffer solutions are usually made up of a mixture of the salt of a weak acid and the acid itself in various proportions, *e.g.*, sodium acetate and acetic acid. In a solution of this mixture we have mainly sodium ions and acetate ions. There will also be some hydrogen and hydroxyl ions. There is, however, a large excess of acetate ions owing to the presence of the well-ionised sodium acetate. If hydrogen ions are added to this solution they combine with the acetate ions to give very slightly dissociated acetic acid

$$H^+ + A^- \rightleftharpoons HA$$

$$\frac{[H^+]\,[A^-]}{[HA]} = K.$$

A^- stands for the acetate ion.

Hence there will be little increase in the p_H. The addition of an acid to the buffer solution therefore makes little difference to the p_H value.

The value of the p_H for a mixture of sodium acetate and acetic acid can easily be calculated if the dissociation constant of the acid is known.

Thus, the dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$ at 25° C. Suppose we have a solution containing 0·2 gm.-molecule of

acetic acid per litre, and 0·02 gm.-molecule of sodium acetate per litre. We require to find the p_H of the solution.

We have

$$\frac{[H^+][A^-]}{[HA]} = 1{\cdot}8 \times 10^{-5},$$

or

$$[H^+] = \frac{1{\cdot}8 \times 10^{-5} \times [HA]}{[A^-]}$$

Assuming that the acid, since it is weak, is not dissociated at all, whilst the salt is completely dissociated,

$$[HA] = 0{\cdot}2,$$

$$[A^-] = 0{\cdot}02.$$

$$\therefore\ [H^+] = 1{\cdot}8 \times 10^{-5} \times 10 = 1{\cdot}8 \times 10^{-4}$$

$$p_H = +\log_{10}\frac{1}{[H^+]} = 3{\cdot}74.$$

If the solution contains 0·02 gm.-molecule of acetic acid, and 0·2 gm.-molecule of sodium acetate, we can calculate the p_H in a similar way.

As before,

$$[H^+] = \frac{1{\cdot}8 \times 10^{-5} \times [HA]}{[A^-]}$$

$$[H^+] = \frac{1{\cdot}8 \times 10^{-5} \times 0{\cdot}02}{0{\cdot}2}$$

$$= 1{\cdot}8 \times 10^{-6}$$

$$\therefore\ p_H = +\log_{10}\frac{1}{[H^+]} = 5{\cdot}74.$$

The values of the p_H given in the Table below have been obtained by calculation in this way :—

TABLE XCVI.

Gm.-mol. Acetic Acid per Litre.	Gm.-mol. Sodium Acetate per Litre.	p_H.
0·185	0·015	3·6
0·164	0·036	4·0
0·126	0·074	4·4
0·080	0·120	4·8
0·042	0·158	5·2
0·019	0·181	5·7

These values can be plotted, and the amount of each substance required to give a certain p_H can be calculated (Fig. 184).

It is clear that a solution containing the salt of any weak acid together with the weak acid itself will behave in a similar way to the above, and the following are frequently used as buffer solutions :

Sodium carbonate and sodium bicarbonate.
Disodium hydrogen phosphate and sodium dihydrogen phosphate.
Boric acid and borax.
Citric acid and sodium citrate.
Sodium phthalate and hydrochloric acid.

The effect of adding 1 c.c. of $N/100$ hydrochloric acid to 1 litre of the buffer solution containing 0·2 gm.-molecule of acetic acid per litre and 0·02 gm.-molecules of sodium acetate per litre, of which the p_H has just been found, may be calculated.

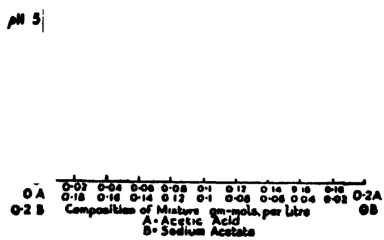


FIG. 184.—p_H Values of Mixtures of Sodium Acetate and Acetic Acid.

The amount of hydrochloric acid added is 0·00001 gm.-molecule. Assuming the acid to be completely dissociated, 0·00001 gm.-molecule of hydrogen ion will be added. The volume change consequent upon the addition will be neglected. The addition of the hydrogen ions causes the formation of more acetic acid from the sodium acetate, and some of the latter will be used up :—

$$\mathrm{Na\bar{A} + HCl = NaCl + H\bar{A}}.$$

Assuming that the acetic acid is not at all dissociated and the sodium acetate is completely dissociated, the reaction will proceed to completion, and all the hydrogen ions will be used up in forming undissociated acetic acid. The amount of undissociated acid thus formed will be 0·00001 gm.-molecule, and the amount of sodium acetate used up will also be 0·00001 gm.-molecule, so that the concentrations $[\mathrm{H\bar{A}}]$ and $[\bar{A}]$ are now 0·20001, and 0·01999 gm.-molecule respectively. Hence, as explained above,

$$[\mathrm{H}^+] = \frac{1{\cdot}8 \times 10^{-5} \times [\mathrm{H\bar{A}}]}{[\bar{A}^-]}$$

$$= \frac{1{\cdot}8 \times 10^{-5} \times 0{\cdot}20001}{0{\cdot}01999}$$

$$= 1{\cdot}801 \times 10^{-4},$$

giving a p_H of $\log_{10} \frac{1}{1\cdot801 \times 10^{-4}} = 3\cdot74$, which is not different from that of the buffer solution itself (3·74, calculated on p. 569).

The effect of adding 1 c.c. of $N/100$ hydrochloric acid to water is much greater. The concentration of $[H^+]$ added is 0·00001 gm.-molecule per litre. Neglecting the ionisation of water, the p_H of this solution would obviously be $\log_{10} \frac{1}{10^{-5}} = 5$. The p_H is therefore changed from 7 to 5.

The above calculations on the p_H of buffer solutions have been very greatly simplified. The assumptions with regard to the degree of dissociation of the weak acid and its salt are certainly not true; but, without this simplification, the calculation is very complicated.

285. Hydrogen Ion Concentration Changes in the Neutralisation of a Strong Acid by a Strong Base.—Quite a different state of affairs is met with here, because the acid, the base, and the salt may all be regarded as completely ionised.

Let us consider the titration of a normal solution of a base with a normal solution of a strong acid, and calculate the p_H of the solution at various stages in the neutralisation. Since both acid and base are strong, there will be no effect of the salt produced on the ionisation, and no hydrolysis.

When 10 c.c. of acid have been added to 50 c.c. of base, and the whole has been made up to 1 litre, there are 40 c.c. of base left. Since the solution was normal there are 40/1,000 gm.-equivalents of base in this volume, so the hydroxyl ion concentration now is 40/1,000, *i.e.*, $0\cdot04 = 4 \times 10^{-2}$. The hydrogen ion concentration is given by the expression

$$[H^+][OH^-] = 10^{-14}.$$

Hence,
$$[H^+] = \frac{10^{-14}}{4 \times 10^{-2}} = 2\cdot5 \times 10^{-13}.$$

When 20 c.c. of acid have been added, there are now 30 c.c. of base left un-neutralised, and hence the hydroxyl ion concentration is now 3×10^{-2}, and the hydrogen ion concentration $3\cdot3 \times 10^{-13}$.

The p_H begins to alter very rapidly in the neighbourhood of the neutralisation point. When 49·5 c.c. of acid have been added, there is 0·5 c.c. of base left, and the hydroxyl ion concentration is $0\cdot5/1{,}000 = 5 \times 10^{-4}$. The hydrogen ion concentration is

$$10^{-14} \div 5 \times 10^{-4} = 2 \times 10^{-11}.$$

Now, when 50·5 c.c. of acid have been added, the hydrogen ion concentration is 5×10^{-4}. There is thus a change in hydrogen ion concentration from 2×10^{-11} to 5×10^{-4} during the addition of

1 c.c. of acid at the neutralisation point. Obviously such a mixture could not be used as a buffer mixture, because the addition of a trace of acid would alter its p_H very much.

The values obtained for the p_H of the solution at various points in the titration are given in the Table below, and are also plotted in the graph (Curve I). This curve is a typical neutralisation curve for a strong acid and a strong base.

TABLE XCVII.

C.c. N NaOH added to 50 c.c. N acid.	$[H^{\cdot}]$.	p_H.
45·0	5×10^{-3}	2·3
49·0	1×10^{-3}	3·0
49·5	5×10^{-4}	3·3
49·9	1×10^{-4}	4·0
49·95	5×10^{-5}	4·3
50·0	1×10^{-7}	7·0
50·05	2×10^{-10}	9·7
50·10	1×10^{-10}	10·0
50·5	2×10^{-11}	10·7
51·0	1×10^{-11}	11·0
55·0	2×10^{-11}	11·7

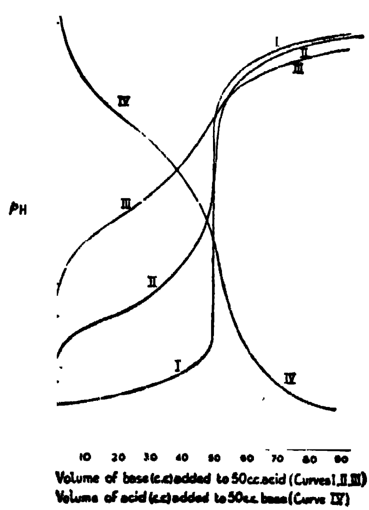


FIG. 185.—Titration of an Acid with a Base.

I. Strong acid—strong base.
II. Weak acid—strong base.
III. Very weak acid—strong base.
IV. Weak base—strong acid.

This curve should be compared with that for the titration of a weak acid by a strong base (Curve II).

The calculation in this case is rather more difficult owing to the fact that the acid is only slightly dissociated, the salt produced by the neutralisation depresses the dissociation of the acid, and the salt is hydrolysed. All three factors have to be taken into account in deriving a mathematical expression for the p_H at any given stage of the neutralisation. In the addition of an alkali to a weak acid, there will be a comparatively large effect on the p_H at first, owing to the combination of the few hydrogen ions present with the added hydroxyl ions of the alkali, but the curve soon flattens out as the salt produced represses the ionisation of the acid. At the equivalence point there is a sudden rise, the sharpness of which will depend upon the degree of hydrolysis of the salt formed. The weaker the acid, the greater the hydrolysis, and the smaller the inflexion of the curve. For a very weak acid, the p_H changes gradually over the whole range. The titration curve is shown in Fig. 185 for the case of a moderately weak acid (II) and a very weak acid (III) and a strong base.

These curves are of importance in connection with electrometric titrations (§ 287). It is clear that the sudden change of p_H for a strong acid and a strong base indicates the end-point of the reaction. Methods of finding p_H values are given in § 277; the one usually employed for this work is the e.m.f. method. It is obvious that the lack of a sudden change in p_H in the case of a weak acid being neutralised by a strong base makes this method of little value in this instance. The curve for a weak base titrated with a strong acid is similar to the Curve II, but starts in the top left-hand corner and finishes at the bottom right-hand corner (Curve IV).

286. Theory of Indicators.—An indicator is a substance which possesses one colour in acid solution and an entirely different one in alkaline solution, *i.e.*, its colour changes with changing hydrogen ion concentration. It follows that it will be more sensitive the smaller the p_H range over which the colour changes.

Ostwald's theory of indicators (1891) supposed that the colour change was due to ionisation. Indicators were supposed to be weak acids or weak bases. They dissolved to give small amounts of hydrogen or hydroxyl ions, and their degrees of ionisation were altered by changes in the concentration of these ions. It was assumed that in the non-ionised state the indicator had a different colour from that of its ions.

Suppose that the indicator is a weak acid HX. It dissociates in water according to the equation

$$HX \rightleftharpoons H^+ + X^-.$$

Addition of hydrogen ions causes the reaction to go from right to left. The hydrogen ion is, of course, colourless, and so it must be the X^- ion that is coloured. Let us see what happens in the case of methyl orange. Methyl orange was supposed by Ostwald to be a very weak base. In solution, therefore, there will be traces of hydroxyl ions and a cation. The undissociated substance is yellow; the colour of the cation is red. The methyl orange dissociates as follows :—

$$\underset{\text{Yellow.}}{X.OH} \rightleftharpoons \underset{\text{Red.}}{X^+} + OH^-.$$

Addition of acid forces the ionisation towards the right, for the hydrogen ions combine with the hydroxyl ions to give the relatively little ionised water. This results in the further ionisation of the indicator, and the liquid is consequently red. On adding alkali, hydroxyl ions are added, which force the ionisation back to the left. Hence, the solution becomes yellow.

Phenolphthalein may be supposed to act as a weak acid. It therefore dissociates as follows :—

$$HPh \rightleftharpoons \underset{\text{Red.}}{Ph^-} + H^+.$$

The undissociated acid is colourless ; the Ph^- ion is red. Addition of hydrogen ions, *i.e.*, addition of acid, forces the dissociation back, and causes the formation of undissociated phenolphthalein which is colourless. Addition of OH^- ions (*i.e.*, addition of alkali) causes diminution of the hydrogen ion concentration, and therefore further ionisation takes place. The colour is thus that of the Ph^- ion, *i.e.*, red.

The fact that phenolphthalein cannot be satisfactorily used for the titration of ammonia or other weak bases is due to the hydrolysis of the salt formed between the ammonia and the indicator. Near the end-point of the titration there would be formed some NH_4Ph, but hydrolysis prevents the formation of Ph^- ions as shown in the equation

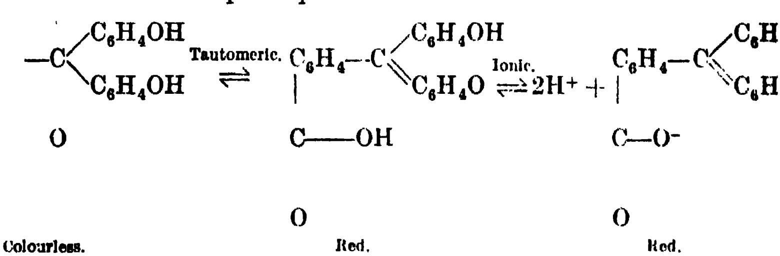
$$NH_4^+ + Ph^- + H_2O \rightleftharpoons HPh + NH_4OH.$$

Hence, the solution remains colourless until a large excess of ammonia has been added.

Methyl orange, being a weak base, is, in a similar way, unsuitable for the titration of a weak acid, but quite satisfactory for a weak base. This point is also brought out by a study of the titration curves (Fig. 185) for a strong acid and a weak base, and a weak acid and a strong base. The indicator works only over a certain p_H range (p. 576). This range may cover the addition of a large quantity of one of the reactants to the other. Thus, in Curve III, the p_H changes from 5 to 8 during the addition of several c.c. of base, and an

indicator changing colour over this range would not give a satisfactory end-point. In Curve I, this p_H change occurs with the addition of a few drops of base only, and hence an indicator changing colour over this range could be used satisfactorily.

It is now generally regarded that the cause of the colour changes of indicators is a tautomeric change in structure rather than ionisation. It is supposed that an indicator solution consists of an equilibrium mixture of two or perhaps more tautomers, one of which exists in acid solution, the other in alkaline solution. At least one of the tautomers is a weak acid or a weak base. Phenolphthalein is a " pseudo-acid." Its salts have the same structure as the acid itself, whilst colourless phenolphthalein is not an acid. The two forms of phenolphthalein are



It can readily be understood how phenolphthalein acts as an indicator. Let H_2Ph be the colourless phenolphthalein,[1] and H_2Ph' the tautomeric coloured form. When sodium hydroxide is added, the salt Na_2Ph' is formed, which is coloured, as the Ph^{--} ion is red, and the Na^+ ion is colourless. So long as the solution is acid, there is no formation of red ions, as the form H_2Ph alone exists in the solution.

It follows from the relationship between p_H and dissociation constant of an acid (p. 550)

$$p_H = \log_{10}\frac{1}{K} + \log_{10}\frac{\alpha}{1-\alpha},$$

that if $\alpha = 0{\cdot}5$, $p_H = \log_{10}\frac{1}{K}$.

When the indicator is half converted from the form existing in acidic to that in basic solutions $[H^+] = K$. This relationship is extremely useful, and is the basis of the determination of the p_H of a solution, whilst it may also be used for the determination of the degree of dissociation of an indicator.

Table XCVIII gives the colour changes of a number of indicators and shows their working range.

[1] Phenolphthalein is probably a dibasic acid, as shown.

TABLE XCVIII.—INDICATORS

(Based upon the Table given in H. S. Taylor's "Treatise on Physical Chemistry," Macmillan, 1924)

Indicator p_H	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Tropaeolin	Flesh	Yellow													
Mauvein	Green	Green-blue	Blue												
Methyl Violet		Green-blue	Blue	Violet											
Tropaelin OO	Red Violet	Flesh-Colour		Yellow											
Methyl Orange				Red		Yellow									
Methyl Red					Rose	Yellowish-red									
Sodium Alizarin-sulphonate			Yellowish Green		Brown		Red								
Cochineal	Yellow					Red-Brown	Lilac								
Rosolic Acid							Brown	Rose	Red						
Litmus					Red	Red Violet	Violet		Blue Violet	Blue					
Phenolphthalein								Colourless		Rose	Red				
Naphthol-benzoin								Brownish Yellow			Green	Green-blue			
Thymol-phthalein										Colourless		Blue			
Alizarin blue S							Greenish Blue		Pale green		Green		Violet	Blue	
Trinitrobenzene													Colourless	Orange	Red
Benzo-purpurin B														Orange	Red

The choice of an indicator for any particular reaction depends largely upon the nature of the p_H neutralisation curve (Fig. 185). In the titration of a strong acid with a strong base (Curve I), the point of exact equivalence is at p_H 7, but the change from p_H 4 to p_H 10 and *vice versâ* is brought about by the existence of as small a quantity as 0·1 c.c. of acid and base respectively in excess. Hence, any indicator changing in colour within the p_H range 4 to 10 could be used without introducing serious error. Even if it changed at p_H 4, the error would only be 0·1 c.c. Consider now the case of the titration of a weak acid by a strong base, *e.g.*, acetic acid by sodium hydroxide. This is typified by Curve II. Actually, sodium acetate is hydrolysed to a certain extent, and, when the p_H of the solution is 7, the point of equivalence has not been reached. The p_H of the solution of sodium acetate is nearly 9. The inflexion of the curve is not so sharp as in Curve I, so that if an indicator were chosen which changes, say, at p_H 4 (*e.g.*, methyl orange), this would be considerably in error. Owing to the broad inflexion, the p_H limits for an error of 0·1 c.c. on the acidic or basic side are reduced to about 8 and 10.

An indicator changing over this range (*e.g.*, phenolphthalein, changing at p_H 9) would have to be used. For the titration of a weak base by a strong acid (Curve IV), the inflexion is broad, and, owing to hydrolysis, the point of equivalence will lie on the acid side. To secure an accuracy of 0·1 c.c. on either side, an indicator changing within the range p_H 3 to 5 must be used.

The following general rules may be given :—

For the Titration of :—	Use.	Which changes at
Strong base and strong acid.	Litmus, or practically any indicator.	
Weak base and strong acid.	Methyl orange.	4
Strong base and weak acid.	Phenolphthalein.	8–9
Weak base and weak acid.	No indicator is really satisfactory.	

287. Electrometric Titrations.—If reference is made to the curves drawn in §§ 284 and 285, representing the p_H changes which occur as a base is neutralised with an acid, it will be noted that there is a sudden change of p_H at the neutralisation point, and that this will be more marked the stronger the acid or base used in the titration. Thus, if a hydrogen electrode (§ 277) were to be immersed in the liquid there would be a sudden change in the e.m.f. at the points of inflexion in the curves. Obviously, if the e.m.f. is measured, and this can be done by means of a potentiometer, it is possible to find the end-point very accurately.

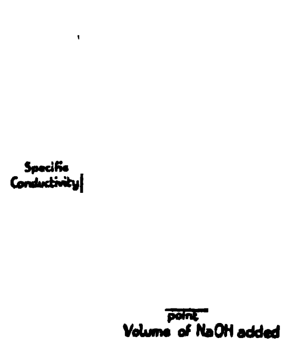


FIG. 186.—Curve for Electrometric Titration.

The method has several advantages over the ordinary indicator method. In the first place, the method can be used with coloured solutions where indicators would be useless, *e.g.*, in the titration of vinegar. Secondly, it is possible to make the method automatic. When the e.m.f. reaches a certain value, a relay is brought into operation which stops the liquid from running from the burette. Electrometric methods are now used extensively for the investigation of precipitation reactions as well as for neutralisation of an acid by a base.

A similar type of titration is the conductivity titration which depends upon the fact that the conductivity of a solution is depen-

dent upon the number of ions present and upon their mobility. Thus, when hydrochloric acid is neutralised with sodium hydroxide, there are present first of all hydrogen ions and chlorine ions. Since the hydrogen ion possesses the greatest mobility of any ion, it follows that the greater part of the conductivity will be due to it. As sodium hydroxide is added, sodium ions are introduced, but hydrogen ions are removed, and the solution at neutralisation contains only sodium and chlorine ions, and will have a considerably smaller conductivity than the original acid. Now, if a little sodium hydroxide is added after the neutralisation, there will be a small concentration of hydroxyl ions, and the conductivity will at once rise, since the hydroxyl ion has the second greatest mobility. Thus, if the conductivity is plotted against the quantity of sodium hydroxide added, a curve is obtained with a sudden break in it. The break occurs at the neutralisation point.

The method has the advantages that it can be used with coloured solutions and will work where no indicator is found to be satisfactory. However, it is necessary to keep the temperature constant, and to have one of the constituents (that which is added) fairly concentrated, to avoid diluting the solution.

288. Solubility Product.—If a solution of an electrolyte is in contact with the solid electrolyte, there are two simultaneous equilibria. The solid is in equilibrium with its solution, and the non-ionised electrolyte in equilibrium with its ions. Thus

$$\underset{\text{solid}}{AB} \rightleftharpoons \underset{\text{dissolved}}{AB} \rightleftharpoons A^+ + B^-.$$

of the Law of Mass Action holds

$$\frac{[A^+][B^-]}{[AB]} = K.$$

But, if there is solid present, the concentration of the undissociated electrolyte is constant, since the undissociated electrolyte is in equilibrium with the solid, which has a constant active mass. Hence, the product of the ionic concentrations will be constant, and

$$[A^+][B^-] = S.$$

This product is called *the solubility product.*

Note that we can only speak of a solubility product when there is excess of solid electrolyte remaining over. The solubility product is not the ionic product under all conditions, but only when there is excess of solid over, *i.e.*, when we are dealing with a saturated solution.

289. Applications of the Concept of Solubility Product.—The effect of an acid in dissolving a sparingly soluble salt was formerly regarded

as the turning out of a weaker acid by a stronger one. But, according to the ionic hypothesis, the hydrogen ions furnished by the stronger acid combine with the anions of the salt, forming the more or less undissociated weaker acid, thus reducing the number of anions. Hence, the solubility product of the sparingly soluble salt is not reached, and it goes into solution. Thus calcium oxalate dissolves in dilute hydrochloric acid. If the salt is represented by CaOx, the solubility product is given by $[Ca^{++}][Ox^{--}] = S$. If dilute hydrochloric acid is added, the hydrogen ions provided by the acid combine with the oxalate ions to give the little-ionised oxalic acid. Thus the concentration of oxalate ions is reduced, and the product $[Ca^{++}][Ox^{--}]$ is now less than S. Hence, the salt dissolves.

If, on the other hand, a solution of calcium oxalate in water is taken, and a solution of oxalic acid, containing a sufficient concentration of oxalate ions is added, calcium oxalate will be precipitated, since the product $[Ca^{++}][Ox^{--}] = S$ will have been exceeded. Similarly, if a solution of calcium chloride is added, precipitation may occur.

Summing up, for a substance AB, for which the solubility product is S, the solid salt can exist in equilibrium with its solution when

$$[A^+][B^-] = S;$$

when

$$[A^+][B^-] < S,$$

the salt dissolves; and when

$$[A^+][B^-] > S,$$

the solution is supersaturated, and salt deposits.

The solubility of the sulphides[1] in acids is governed by similar relationships. The solubility products of some of the metallic sulphides are given in the following Table.

TABLE XCIX.—SOLUBILITY PRODUCTS OF SULPHIDES

Sulphide.	Solubility Product.	Sulphide.	Solubility Product.
MnS (buff) . .	7×10^{-6}	NiS . . .	10^{-27}
FeS . . .	$\sim 10^{-20}$	PbS . . .	4×10^{-28}
MnS (green) . .	6×10^{-22}	CdS . . .	$\sim 10^{-28}$
Tl_2S . . .	5×10^{-24}	CuS . . .	3×10^{-42}
ZnS . . .	10^{-24}	Hg_2S . . .	10^{-47}
CoS . . .	2×10^{-27}	Ag_2S . . .	10^{-50}
		HgS . . .	3×10^{-54}

[1] It is only possible to give a simplified account here. For a fuller discussion of the question see A. J. Mee, "The Precipitation of Sulphides," *School Science Review*, June, 1937.

Zinc sulphide dissolves in dilute hydrochloric acid, but only slightly in dilute acetic acid, whilst manganous sulphide dissolves readily even in dilute acetic acid. This can be explained as follows: The manganous sulphide has a solubility product of 7×10^{-6}. When dilute acetic acid is added, quite a small concentration of hydrogen ions is added, but these combine with sulphide ions to give the very little ionised hydrogen sulphide. Since the number of sulphide ions present is comparatively large (compared with other sulphides), the product of hydrogen and sulphide ion concentrations is sufficient to exceed the solubility product of sulphuretted hydrogen,[1] and so the compound is produced. It may remain in solution, or may be partly given off as gas. In any case, sulphide ions are progressively removed from the solution, and all the manganous sulphide dissolves.

The solubility product of zinc sulphide is 10^{-24}. Here the solubility product is much smaller than that of manganous sulphide. The addition of dilute acetic acid is insufficient to provide hydrogen ions in great enough concentration to reach the solubility product of hydrogen sulphide, and so the sulphide does not dissolve in dilute acetic acid. A little of it will dissolve, but an equilibrium will rapidly be reached. Dilute hydrochloric acid, however, contains sufficient hydrogen ions to cause the solubility product of sulphuretted hydrogen to be reached, and hence the undissociated substance is formed and the sulphide dissolves.

Mercury sulphide, with a solubility product of 3×10^{-54}, cannot provide enough sulphide ions to exceed the solubility product of hydrogen sulphide, even if a very strong acid is used. Hence, it is insoluble in all acids.

An alternative explanation is that, on addition of hydrochloric acid to mercuric sulphide, we have the equilibria

$$HgS \rightleftharpoons Hg^{++} + S^{--},$$
$$S^{--} + 2H^+ \rightleftharpoons H_2S.$$

[1] Strictly speaking, hydrogen sulphide has not a solubility product in the sense of the definition given above. It is a weak dibasic acid which ionises in two stages:—

$$H_2S \rightleftharpoons H^+ + HS^-,$$
$$HS^- \rightleftharpoons H^+ + S^{--}.$$

The dissociation constants are (§ 271):—

$$\frac{[H^+][HS^-]}{[H_2S]} = 10^{-7}; \quad \frac{[H^+][S^{--}]}{[HS^-]} = 10^{-15}.$$

Hence,
$$\frac{[H^+]^2[S^{--}]}{[H_2S]} = 10^{-22}.$$

In a saturated solution of the gas at 25° C. (to which temperature the above figures refer) $[H_2S] = 0{\cdot}1$, and hence $[H^+]^2[S^{--}] = 10^{-23}$. This may be regarded as the solubility product of hydrogen sulphide.

The maximum concentration of H^+ that can be added will not reduce $[S^{--}]$ so low that the solubility product of mercuric sulphide cannot be reached.

The precipitation of sulphides is governed by similar considerations. It is known that the sulphide ion concentration in an $M/5$ solution of hydrochloric acid, saturated with the gas, is about 10^{-22}. For precipitation to occur, the solubility product of the sulphide must be exceeded. Suppose the solutions of the metallic salts used are approximately $M/10$; then the concentration of metal ion in the solution must be about 0·1 when each molecule of salt gives one metal ion. Hence, the product [Metal] $[S^{--}]$ in such a solution of a metallic salt in hydrochloric acid, saturated with hydrogen sulphide, is $10^{-22} \times 0{\cdot}1 = 10^{-23}$. Those metals with sulphides of solubility product less than 10^{-23} will be precipitated. Thus, cupric sulphide has the solubility product 3×10^{-42}. This value is more than reached if a 0·1 M solution of cupric chloride in 0·2 M hydrochloric acid is treated with hydrogen sulphide. Indeed, the value of the product is then 10^{-23}. Hence, cupric sulphide is precipitated. Certain metals lie on the border line. Cadmium sulphide has a solubility product about 10^{-28}. If the conditions outlined above hold, the sulphide will be precipitated on passing hydrogen sulphide through a solution of cadmium chloride in $M/5$ hydrochloric acid. If, however, the hydrochloric acid used is stronger, the value of $[S^{--}]$ in the solution is less (since $[H^+]^2$ $[S^{--}]$ must be constant), and the solubility product may not now reach 10^{-28}, especially if the solution is weak in cadmium ions. Zinc sulphide has a solubility product of 10^{-24}. This is just on the border line. In aqueous solution, $[H^+]^2$ $[S^{--}]$ is 10^{-23}, and it has been shown that $[S^{--}]$ is 10^{-15}. If hydrogen sulphide is passed through an $M/10$ aqueous solution of zinc sulphate, the product $[Zn^{++}]$ $[S^{--}]$ would be 10^{-16}. This is greater than the solubility product of zinc sulphide, and hence zinc sulphide is precipitated. In $M/5$ hydrochloric acid $[S^{--}]$ is 10^{-22}. If $M/100$ zinc chloride in $M/5$ hydrochloric acid were to be treated with hydrogen sulphide, the product $[Zn^{++}]$ $[S^{--}]$ would be 10^{-24}, and the sulphide would just be precipitated. In stronger acid solutions $[S^{--}]$ is less than 10^{-22}; and so in solutions of zinc chloride of concentration less than about $M/5$ no precipitation occurs. If some substance is present in the solution which can buffer it, *e.g.*, acetate ions, the hydrogen ions of the hydrochloric acid are removed as undissociated acetic acid, and so the value of $[S^{--}]$ will rise almost to that found in aqueous solution. Thus, in presence of sodium acetate, zinc sulphide is readily precipitated.

The concentration of sulphide ions in an $M/10$ ammonium

ulphide solution is 2×10^{-6}. Nearly all sulphides have solubility roducts considerably less than this, so they are precipitated, even rom very dilute solutions, by this reagent.

The use of a mixture of ammonium chloride and ammonium ydroxide to precipitate aluminium, iron and chromium in qualitaive analysis is explained in this way. The hydroxides of the metals f the ammonium sulphide and ammonium carbonate groups (and agnesium) would be precipitated by ammonium hydroxide, the olubility product $[M^+]\,[OH^-]^x = S$ being exceeded, owing to the ydroxyl ions being supplied by the ammonia. If, however, mmonium chloride is added to the ammonium hydroxide, its onisation is considerably repressed, since the concentration of mmonium ions has been increased, and $[NH_4^+]\,[OH^-]$ must remain onstant. Thus, there is a great decrease in the concentration of ydroxyl ions in the solution, and the solubility products of the ydroxides of the metals of the above groups and magnesium are ow not reached.

The validity of the theory of solubility product has sometimes een called in question. There seems no doubt that it holds ccurately, or fairly accurately, for sparingly soluble salts, but that or saturated solutions of substances which are moderately, or easily, oluble in water, there are considerable deviations. It has been ound, however, that the solubility product for a given substance is ot always constant. This is probably due to the fact that ions dded to the saturated solution of a salt AB may exert some lectrostatic effect on the ions A and B, making the solubility roduct either greater or less. The solubility product is more early constant when activities are substituted for concentrations § 161).

SUMMARY

The application of the Law of Mass Action to the equilibrium in a inary electrolyte leads to the result

$$K = \frac{\alpha^2}{v(1 - \alpha)},$$

where v is the dilution and α the degree of dissociation. K is a constant alled the "dissociation constant." The Law is known as the Ostwald Dilution Law. Many substances do not obey it, particularly strong lectrolytes. Investigation of the reasons for the failure of the Law ed to the formulation of the theory of complete dissociation, which ssumes strong electrolytes to be completely dissociated at all concenrations, differences in conductivity being due to electrostatic interction between the ions. This theory leads to an equation identical in orm with that of Kohlrausch, *i.e.*,

$$\Lambda_\infty - \Lambda_v = KC^{\frac{1}{2}}.$$

The hydrogen ion concentration of a solution is usually expressed as the

$p_H = -\log_{10}[H^+]$. In pure water there is an equilibrium between hydrogen and hydroxyl ions, governed by the equation $[H^+][OH^-] = K_w = 10^{-14}$ at 25° C. When a salt is dissolved in water, reaction takes place between the two substances, and the solution is usually acidic or alkaline. This is known as hydrolysis. The salt of a strong base and a weak acid will give an alkaline solution ; that of a strong acid and a weak base an acid solution. The degree of hydrolysis, h, is the fraction of the original salt hydrolysed, and the hydrolysis constant K_h is given by $\frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrolysed salt}]}$, the quantities in square brackets indicating concentrations. The degree of hydrolysis can be determined by several methods, including (1) distribution method, (2) conductivity method, (3) colligative property method, (4) catalysis method, (5) e.m.f. method, and (6) the use of indicators.

Buffer solutions, or solutions of reserve acidity or alkalinity, are prepared by mixing the sodium salt of a weak acid with the acid itself. Addition of $[H^+]$ to a buffer solution makes very little difference to the p_H. An indicator is a substance which exists in two tautomeric forms, one of which exists in acid, the other in alkaline solution. The two forms are differently coloured. The choice of an indicator for any given acidimetric titration depends upon the strength of the acid and base used.

The solubility product of a salt is the ionic product in saturated solution. When this is exceeded, precipitation takes place ; when it is not reached, solution occurs.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 36.—Carry out an electrometric titration of sodium hydroxide by hydrochloric acid.

Experiment 37.—Determine the degree of hydrolysis of aniline hydrochloride by the distribution method (p. 564).

SUGGESTIONS FOR FURTHER READING

GLASSTONE, S. "The Electrochemistry of Solutions." (*Methuen*, 1930.)

MEE, A. J. "The Precipitation of Sulphides." *School Science Review*, June, 1937.

QUESTIONS

(1) In what ways does the failure of Ostwald's Dilution Law to explain the behaviour of strong electrolytes necessitate revision of Arrhenius' hypothesis ?

(2) What is meant by the term "degree of hydrolysis" ? How would you determine the degree of hydrolysis of aniline hydrochloride ?

(3) What methods are available for the quantitative determination of hydrolysis ?

(4) How may the ionic product for water be determined ? Why is this an important figure ?

(5) What do you mean by the term "solubility product" ? Show how the concept can be used to explain many of the processes of qualitative analysis.

(6) How would you attempt to verify the constancy of the solubility product for silver chloride ?

(7) Calculate the p_H at 25° C. of mixtures of
(a) 164 c.c. $N/5$ acetic acid and 36 c.c. $N/5$ sodium acetate.
(b) 59 c.c. $N/5$ acetic acid and 141 c.c. $N/5$ sodium acetate.
(c) 9 c.c. $N/5$ acetic acid and 191 c.c. $N/5$ sodium acetate.
The dissociation constant of acetic acid at 25° C. is $1 \cdot 8 \times 10^{-5}$.

(8) The variation of the dissociation constants of acetic acid (K_a) and ammonia (K_b), with temperature are given in the following Table :—

Temp., °C.	18°	100°	156°
K_a . .	$1 \cdot 72 \times 10^{-5}$	$1 \cdot 35 \times 10^{-5}$	$6 \cdot 28 \times 10^{-6}$
K_b . .	$1 \cdot 83 \times 10^{-5}$	$1 \cdot 11 \times 10^{-5}$	$5 \cdot 36 \times 10^{-6}$

Calculate the degree of hydrolysis of $M/10$ solutions of ammonium acetate at 18° C., 100° C. and 156° C. What effect has temperature on the degree of hydrolysis ?

(9) From the data given in Question 8, calculate the heat of ionisation of acetic acid and of ammonium hydroxide.

(10) Williams and Soper (*J.C.S.*, 1930, 2469) determined the hydrolysis constant of *o*-chloroaniline hydrochloride by the distribution method. The distribution coefficient of the free amine between water and benzene was first determined. 1,000 c.c. of water were used, and 60 c.c. benzene (counted as 59 c.c. to make up for solution of benzene in the aqueous layer). The following were the results :—

Wt. of $R.NH_2$ put in gms.	Wt. of $R.NH_2$ in 59 c.c. Benzene, gms.
2·6128	2·293
3·0647	2·683
1·3380	1·166
1·2000	1·053

Calculate the distribution coefficient and obtain its mean value. In the second part of the experiment unequal amounts of hydrochloric acid and the amine were mixed in the aqueous layer (1,000 c.c.) and shaken with 60 c.c. benzene. c_1 and c_2 are the total initial molar concentrations of hydrogen chloride and the amine respectively.

c_1.	c_2.	Wt. of RNH_3Cl from 50 c.c. Benzene, gms.
0·01206	0·01122	0·9800
0·02671	0·02569	1·7694
0·02896	0·02281	1·5084
0·01853	0·01534	1·1706

Calculate the hydrolysis constant K_h from each of these readings, and find its mean value.

Assuming that K_w at the temperature of the experiment (25° C.) is $1 \cdot 005 \times 10^{-14}$, calculate the dissociation constant of *o*-chloroaniline hydroxide.

CHAPTER XIV

ACIDS, BASES, AND SALTS

290. Definition of an Acid.—The best definition of an acid is "*a compound containing hydrogen which can yield hydrogen ions (free or solvated) either by itself, or when dissolved in water.*" This is the best because most of the reactions and properties which characterise an acid are due to hydrogen ions. It is obvious that here the acid salts are included as acids because they do, under ordinary circumstances, give hydrogen ions when dissolved in water. The classical definition of an acid as a substance which, when treated with a solution of an alkali, gives a salt and water only, still holds good. The latter is a delicate test for a substance yielding hydrogen ions. It excludes water but includes acid salts, amphoteric hydroxides, and pseudo-acids.

291. Bases, and the Extended Theory of Acids and Bases.—The classical definition of a base is "*a substance which will react with acids giving a salt, or a salt and water only.*" All bases which are soluble in water give rise to hydroxyl ions in aqueous solution.

Hydroxyl ions very readily combine with hydrogen ions to form undissociated water. This has led to a rather extended definition of the term "base" as a "*substance that will combine with hydrogen ions.*"

Now, if we accept this definition, we are forced to the conclusion that water itself is a base, because we know that the hydrogen ion is very largely solvated in aqueous solution. The water has combined with the hydrogen ion. It is true that water does show certain basic powers. Thus, although water is a much weaker base than ammonia, it can compete with it for the proton, a fact which is shown by the partial hydrolysis of ammonium salts in aqueous solution right down to ammonia, thus :—

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+.$$

Extending the definition of a base to charged bodies, *i.e.*, ions, the anions of all weak acids are bases, because they are not easily parted from the hydrogen ion. When a weak acid is dissolved in water, the ionic reaction taking place is

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-.$$

The anion, A^-, is called the conjugate base of the weak acid HA.

* **292. Basicity of Acids.**—It is difficult to give a precise definition of basicity. The best definition is "*the basicity of an acid is the number of hydrogen ions that can be formed from one molecule of the acid.*" Thus, acetic acid, although it contains four atoms of hydrogen, is monobasic, because one molecule of the acid furnishes only one hydrogen ion. It is true that it is possible for acetic acid to form two distinct potassium salts, CH_3COOK and $CH_3COOK.CH_3.COOH$, but its general behaviour is that of a monobasic acid. Sulphuric acid, too, forms definite crystalline compounds with sodium hydroxide, of the formulæ $NaH_3S_2O_8$, $Na_2H_2S_2O_8$, and $Na_3HS_2O_8$, in addition to the usual Na_2SO_4 and $NaHSO_4$. If the definition of basicity were taken as the number of distinct compounds that could be formed between the acid and sodium hydroxide, sulphuric acid would appear to be pentabasic. Actually, it is dibasic. The reason for the existence of the above compounds is that they are molecular compounds (p. 151). They may be written

$$NaH_3S_2O_8 = NaHSO_4.H_2SO_4.$$
$$Na_2H_2S_2O_8 = Na_2SO_4.H_2SO_4.$$
$$Na_3HS_2O_8 = Na_2SO_4.NaHSO_4.$$

In solution these compounds break down into their constituents, giving Na_2SO_4, $NaHSO_4$ and H_2SO_4 (before dissociation occurs). In solution the only compounds in the above list that can have individuality are Na_2SO_4, $NaHSO_4$, and H_2SO_4, so that actually only two true salts can be made with the acid and base.

To determine the basicity of an acid, the usual method, where the molecular weight is unknown, is to see how many true salts can be formed from the acid and sodium or potassium hydroxide. Molecular compounds must be excluded. Thus, to determine the basicity of an acid, a given volume of it is taken, and exactly neutralised with sodium hydroxide solution, the volume required being noted. The solution of the salt obtained is evaporated to crystallisation, and the characteristics of the crystals are noted. Now, the same volume of acid as was used previously is taken, and only half the caustic soda used before is added, thus half neutralising the acid. Different crystals may be obtained on evaporating this solution to crystallisation. Other fractions, or multiples, of the volume of sodium hydroxide used should be tried, according to the suspected basicity.

If the molecular weight of the acid is known, its basicity can usually be found by direct titration with sodium hydroxide of known strength. Thus for every molecular weight of the acid we shall use up 40 gms. of caustic soda if it is monobasic, 80 gms. if it is dibasic, and, in general, 40 *n* gms. if it is *n*-basic. This method can be used if a suitable indicator can be found. Actually, the stage of

formation of the normal salts of most tribasic acids is beyond the range of all indicators.

Another useful method which has yielded some interesting results is the thermal method. The molecular weight of the acid must be known If a monobasic acid is taken, say hydrochloric acid, and it is exactly neutralised with sodium hydroxide, a certain amount of heat is liberated—the heat of neutralisation—which is approximately constant for all monobasic acids of reasonable strength, and amounts to about 13,700 gm.-cals. per gm.-mol. If, now, we take one molecular weight of a dibasic acid, and add one molecular weight of caustic soda, a certain amount of heat will be evolved, corresponding to the formation of the acid salt, and if we now again add the same quantity of sodium hydroxide, more heat will be given out, the normal salt being formed. Further addition of sodium hydroxide does not result in the liberation of any more heat, as the heat of neutralisation is practically independent of dilution. If an acid is tribasic, the effect of adding to one gm.-mol. of it three separate portions of one gm.-mol. each of sodium hydroxide will be the liberation of three separate amounts of heat. Further addition of the base merely dilutes the salt formed, and the heat of dilution is negligible if the solution is already dilute.

The results of this method, of course, apply only to acids in solution, and they are likely to be complicated by hydrolysis. Thus the solution of hydrogen sulphide in water, known as hydrosulphuric acid, appears to be monobasic. When one gram-molecule of hydrosulphuric acid is mixed with one gram-molecule of sodium hydroxide, both in dilute solution, the heat liberated is 7,740 gm.-cals. If a further gram-molecule of sodium hydroxide is added, there is practically no heat evolved, whereas, if the acid were dibasic, as expected, there should be a further quantity given off. The reason for the apparent monobasicity of this acid is that hydrolysis occurs and that Na_2S cannot exist in dilute solution.

$$Na_2S + H.OH = NaSH + NaOH.$$

A classical example of the use of this method was in the investigation of the basicity of periodic acid. If periodic acid is titrated against strong bases, it is monobasic when methyl orange is used as indicator, but dibasic with thymolphthalein. The formula of the acid is regarded as HIO_4, or $H_5IO_6(HIO_4, 2H_2O)$. Thus, when chlorine acts on potassium iodate in the presence of caustic potash, a salt is formed with the formula KIO_4, whereas similar treatment of the sodium compound gives $Na_2H_3IO_6$. Thomsen found the amount of heat evolved when a given weight of the acid (taken for these experiments as H_5IO_6, though the molecular

weight was unknown) was neutralised with caustic potash, and found the following values :—

$$H_5IO_6 + KOH \quad . \quad . \quad 5{,}150 \text{ gm.-cals.}$$
$$H_5IO_6 + 2KOH \quad . \quad . \quad 26{,}590 \quad ,,$$
$$H_5IO_6 + 3KOH \quad . \quad . \quad 29{,}740 \quad ,,$$

The figures refer to the total amount of heat evolved.

Thus, there is very little further heat evolved when the third gm.-mol. of caustic potash is added. The data would indicate, then, that the acid is dibasic, and the formula was written $H_2(H_3IO_6)$. Moreover, the figures show that much more heat is given out on addition of the second gm.-mol. than on addition of the first. To explain this, it was assumed that the salt $KH(H_3IO_6)$, which would be formed on the first addition, was unstable and lost water, becoming KIO_4, and that the low value is due to the heat used up in this breakdown. The second addition results in the formation of $K_2(H_3IO_6)$, water being again taken up. The fact that periodic acid is dibasic has recently been confirmed by Rae (*J.C.S.*, 1931, 876) by conductometric titration (§ 287).

Ostwald discovered the empirical rule that for the sodium salt of a monobasic acid the difference between the equivalent conductivity at a dilution of 32 litres, and at 1,024 litres, was about 10 units; for the sodium salt of a dibasic acid it was 20 units; for the sodium salt of a tribasic acid 30 units, and so on. The law was tested with pyridine mono-, di-, tri-, tetra- and penta-carboxylic acids for which the differences of the equivalent conductivity of the sodium salts at dilutions of 32 and 1,024 litres were 10·4, 19·8, 31·0, 40·4, and 50·1 respectively.

The application of this method to hydrofluoric acid is interesting. The difference in the equivalent conductivity of sodium fluoride at dilutions of 32 and 1,024 litres is 20·8, thus indicating that the acid is dibasic, a conclusion supported by many other facts.

It has been shown that as a rule only polybasic acids can break down on heating into an anhydride and water (iodic acid is an exception, $2HIO_3 \rightarrow H_2O + I_2O_5$ on heating to 240° C.), whereas the monobasic acids have to be more drastically treated to obtain the anhydride. Thus succinic acid readily yields an anhydride, merely by heating, whereas acetic acid has to be converted into sodium acetate, and this has to be distilled with acetyl chloride to form acetic anhydride. This method is sometimes useful in determining whether an acid is monobasic.

293. Strengths of Acids.—Acids vary a good deal in their possession of acidic properties. If asked to classify acids according to their strengths, we should probably think at once that the acid that was most corrosive was strongest. This view, however, is entirely

erroneous. Very little information can be obtained about the relative strengths of acids by comparing the rates with which they react with metals. Experiments of this kind can be carried out, but they do not give correct results. Our general ideas on the stengths of acids deduced from their corrosive powers would lead us to believe that sulphuric acid was a stronger acid than hydrochloric, and our views would be confirmed by the fact that sulphuric acid will displace hydrochloric acid from common salt. But then, we have to take into account that phosphoric acid will displace hydrochloric acid from common salt too. Can phosphoric acid be stronger than hydrochloric acid? Moreover, hydrochloric acid will displace sulphuric acid from sodium sulphate if excess of strong hydrochloric acid is added to a saturated solution of sodium sulphate. It is clear that values for the relative strengths of acids cannot be based on experiments such as these. The reason why hydrogen chloride is turned out of common salt by the acids like sulphuric and phosphoric is because it is so volatile compared with them. Actually, when sulphuric acid is added to common salt, a reversible reaction takes place:—

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$

and if the system were not heated the reaction would be predominantly towards the left. When the system is heated, however, hydrogen chloride is removed because it is so volatile, and, consequently, the reaction proceeds towards the right-hand side of the equation. Note that it is not because sulphuric acid is any stronger than hydrochloric; indeed, the reverse is the case. The reaction is just a consequence of the Law of Mass Action.

It is obvious that a reaction such as the above, where the *equilibrium is altered*, cannot be used to decide the strength of an acid. However, if the position of the equilibrium in the initial reaction given, *viz.*,

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$

could be judged, the information gained would show how far sulphuric acid is capable of turning out hydrochloric acid from its combination with sodium hydroxide, and hence how strong the acid is. It must be noted that the equilibrium must not be disturbed (as it was when the system was heated).

The problem is, then, to find how a base distributes itself between two acids. If a quantity of base insufficient to neutralise a mixture of two acids is taken, it will obviously combine to a greater extent with the stronger of the two acids, and to a lesser extent with the weaker. Physical methods will have to be used to study the equilibrium, as any chemical methods will disturb it.

A method of solving the problem was found in the determination of the volume change which takes place when a base distributes itself between the acids. Let us take the case of the determination of the relative strengths of nitric and dichloracetic acids by this method. If we mix one equivalent of nitric acid with one of dichloracetic and then add one equivalent of caustic potash, the base will distribute itself between the two acids according to their strengths, or, to use an older term, their "avidities" for the base. We thus have to find the position of the equilibrium in the reaction

$$CHCl_2COOK + HNO_3 \rightleftharpoons KNO_3 + CHCl_2COOH.$$

It is found that when one gm.-mol. of caustic potash is neutralised by one gm.-mol. of nitric acid, both in dilute solution, there is an increase in volume of 20 c.c.

When, however, one gm.-mol. of caustic potash is neutralised by one gm.-mol. of dichloracetic acid, again in dilute solution, there is an increase in volume of 13 c.c.

If now the above reaction went all the way to the right, there would be a net increase in volume of $20 - 13 = 7$ c.c.

Actually, when the reaction is carried out, the increase in volume is 5·67 c.c. Hence, the reaction has gone from left to right to the extent of $5{\cdot}67/7 \times 100$ per cent. = 81 per cent.

Thus, the nitric acid has taken about 80 per cent. of the base, and the dichloracetic acid 20 per cent. We can therefore conclude that nitric acid is four times as strong as dichloracetic.

The observation of any physical change taking place on neutralisation will serve the purpose just as well. The amount of heat evolved when a base is allowed to act upon an excess of mixed acids has been used. Thus, to find the relative strengths of sulphuric and hydrochloric acids in dilute solution, the heats of neutralisation of sulphuric and hydrochloric acids separately must be known, and the amount of heat liberated when one equivalent of caustic soda is added to a mixture of one equivalent of each of the acids must be determined. Thus the heat of neutralisation of hydrochloric acid by sodium hydroxide is 13,700 gm.-cals., whilst that of sulphuric acid is 15,700 gm.-cals. Consider the reaction

$$KCl + \tfrac{1}{2}H_2SO_4 \rightleftharpoons \tfrac{1}{2}K_2SO_4 + HCl.$$

If it were to go entirely to the right there would be an evolution of heat of 2,000 gm.-cals. according to Hess's Law. Actually, however, only 700 gm.-cals. are evolved, so that when equilibrium is attained the reaction has only gone to the right to the extent of 700/2,000 = 0·35. The relative avidities of the acids must be 0·65/0·35 = 100/54. If hydrochloric acid is taken as 100, the strength of sulphuric acid will be 54.

Other physical changes can be used for this purpose. For example, Ostwald used the small changes in refractive index on neutralisation to determine the relative strengths of acids. The method of calculation is similar to the above.

It is found that acids catalyse the saponification of esters, and the inversion of cane-sugar. This is not, however, an ordinary case of catalysis, for the rate of reaction is dependent upon the quantity of acid present and upon its strength. As a matter of fact, the reaction is very complicated, and will be discussed in greater detail later (pp. 595, 708). When cane-sugar is acted upon by a dilute acid, hydrolysis takes place, and a mixture of glucose and fructose in equivalent amounts is formed.

$$\underset{\text{cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose.}}{C_6H_{12}O_6} + \underset{\text{fructose.}}{C_6H_{12}O_6}.$$

Cane-sugar is dextro-rotatory, but the mixture of glucose and fructose has a resultant lævo-rotation. Hence, the course of the reaction can be conveniently followed by noting the change in rotation. A solution of cane-sugar (say 15 or 20 per cent.) is mixed with an equal volume of the acid, the strength of which is to be measured, which should be in normal solution. The mixture is put into the polarimeter tube, maintained at a constant temperature, and the rotation is noted at given times. The tube is allowed to stand for some time until the reaction is complete, and the final reading is taken. The reaction is pseudo-unimolecular, so that the unimolecular equation holds (§ 163). If r_0 is the initial rotation, r_n the rotation at time t_n, and r_∞ the final rotation, the velocity constant k is given by

$$k = \frac{2 \cdot 303}{t_n} \log_{10} \frac{r_0 - r_\infty}{r_n - r_\infty}.$$

The experiment is now repeated using another acid. The order of the velocity constants obtained for a series of different acids gives the order of their strengths.

To determine the strengths of acids using the method of ester catalysis, it is most convenient to use methyl acetate as the ester, as it is fairly rapidly hydrolysed at room temperatures. Acids of $N/2$ strength may be used. Suppose we are dealing with hydrochloric acid. 100 C.c. of the $N/2$ acid are taken, and placed in a corked flask in a thermostat. After half an hour, 5 c.c. of methyl acetate are added, and the time noted. Immediately, 5 c.c. of the mixture are withdrawn and run into 20 c.c. of distilled water. The mixture is then titrated with $N/10$ caustic soda, or baryta, using phenolphthalein as indicator. This procedure is repeated at intervals of about ten minutes, the time of withdrawal being always noted. To

obtain the final reading, the flask is left for two days in the thermostat and then the liquid is titrated as before. The reaction may be regarded as unimolecular with respect to the methyl acetate, since the hydrochloric acid is taken in such great excess. If t_0 is the initial titre, t_a the titre after time a, and t_∞ the final titre, the velocity constant is given by

$$k = \frac{2 \cdot 303}{a} \log_{10} \frac{t_0 - t_\infty}{t_a - t_\infty}.$$

As before, the experiment is repeated with another acid, and the order of the values of k given by a series of acids is the order of their strengths.

Arrhenius noticed in 1884 that the order of the strengths of acids obtained by the above methods was the same as the order of their electrical conductivity in equivalent solution, and, indeed, there is fair quantitative agreement between the values obtained by the different methods. The following Table shows this.

TABLE C.—STRENGTHS OF ACIDS

Acid.	Method.			
	Thermochem.	Sugar Inversion.	Ester Catalysis.	Conductivity.
Hydrochloric	100	100	100	100
Nitric	100	100	91·5	99·6
Sulphuric	49	53	54·7	65·1
Oxalic	24	18·6	17·4	19·7
Orthophosphoric	13	6·2	—	7·3
Monochloracetic	9	4·8	4·3	4·9
Tartaric	5	—	2·3	2·3
Acetic	3	0·4	0·35	0·4

From this, it is very probable that the strength of an acid is in some way bound up with its electrical conductivity. Now, in the case of an acid, HX, the conductivity is due both to the hydrogen ions and the anions, X. But the mobility of the hydrogen ion is considerably greater than that of any anion, and hence we can say that the conductivity is very roughly proportional to the hydrogen ion concentration. An acid, like hydrochloric acid, owes the greater part of its conductivity to the hydrogen ions. Hence, it was supposed that the strength of an acid was measured by the hydrogen ion concentration in its solution. An acid which was almost completely dissociated at moderate dilutions would be a

strong acid, whereas one like acetic acid, which still had a good proportion of undissociated molecules even at a dilution of $N/20$, was weak. Many of the methods described above for the determination of the strengths of acids are merely methods for determining hydrogen ion concentration. Thus, the inversion of cane-sugar, and the hydrolysis of methyl acetate, are catalysed by hydrogen ions, and by measuring the rates of these reactions we are merely measuring the hydrogen ion concentration in the solution.

It is obvious that any of the methods of determining hydrogen ion concentration, described in § 277, will suffice for the determination of the strength of an acid if this theory is correct. The value of the dissociation constant K (§ 271) of the acid will be a good index of the strength of an acid.

A point to be noted is that, if the strength of an acid is measured by the concentration of hydrogen ions in its solution, the strengths of all acids tend to become the same as the solutions are progressively diluted. At infinite dilution, all acids would be completely ionised, and their strengths would then be the same. The apparent paradox that an acid gets stronger as it is diluted is explained in this way. It should also be noted that the strengths of acids should be compared in every case in solutions of the same normality. This applies to all methods of determining the strength. Otherwise, of course, anomalous results would be obtained.

Similarly, it has been proposed to measure the strength of a base by the hydroxyl ion concentration of its solution. The Table below gives the degree of dissociation (a measure of the hydroxyl ion concentration) of several bases in $N/2$ and $N/1{,}000$ solution.

TABLE CI.—DEGREE OF DISSOCIATION OF BASES

	$N/2$.	$N/1{,}000$.	Relative Strength in $N/1{,}000$ solution.
Potassium hydroxide, KOH	0·826	0·981	100
Sodium hydroxide, $NaOH$	0·795	0·966	98
Barium hydroxide, $Ba(OH)_2$	0·90 ($N/10$)	0·977	99
Methylammonium hydroxide, CH_3NH_3OH	0·313	0·500	51
Ammonium hydroxide, NH_4OH	0·0068	0·141	14
Anilinium hydroxide, $C_6H_5NH_3OH$	0·000030	0·00068	0·068

These figures have been arrived at from conductivity measurements.

It will be seen that there are two well-defined classes—the strong and the weak bases respectively.

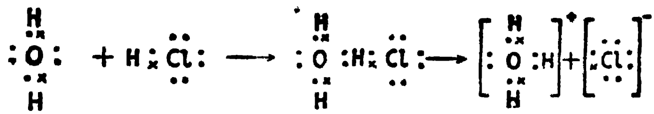
294. Hydration of the Hydrogen Ion, and Modification of the Hydrogen Ion Theory of Strengths of Acids.—Although we have stated that it was proposed to measure the strength of an acid by the concentration of hydrogen ions produced in its aqueous solution (if we are dealing with aqueous solutions of acids), this statement requires some qualification. In the presence of water, the hydrogen ion is invariably solvated, and carries about with it a certain quantity of water. The amount of this has been variously stated, but we may take the simplest case and say that the hydrogen ion travels about accompanied by one water molecule. Actually, then, we are not dealing with hydrogen ions themselves, but with ions of the formula $[H_3O]^+$.

That hydrogen ions are solvated in aqueous solution can be shown by several methods. In the first place, transference experiments indicate that the hydrogen ion must be solvated. Washburn carried out transport-number experiments in which a non-electrolyte such as sugar (raffinose) was dissolved in the solution of the acid used in the electrolysis. On passing the current, the sugar, of course, did not move, and yet it was found after the experiment that the concentration of sugar was greater round one electrode than the other, because unequal quantities of water had been carried by the anion and by the cation. The work of Washburn has since received confirmation from the experiments of Taylor and Sawyer, who used urea as a reference substance instead of raffinose. Experiments of this kind show that nearly all ions are hydrated.

Goldschmidt carried out experiments on the conductivity of dilute solutions of hydrogen chloride in alcohol, and the effect of addition of water to these solutions. He found that the addition of a small amount of water was sufficient to decrease the conductivity considerably, and that this decrease could not be accounted for by any increase in the viscosity of the alcohol, or alteration of the dielectric constant. It must therefore be due to an increase in size of the ions, thus decreasing their mobility. This could readily be brought about by the taking up of water molecules, and a small amount of water would be sufficient to supply the necessary molecules.

Other reasons of a theoretical nature can readily be given for the hydration of the hydrogen ion. We know that, for a substance to ionise, it must be an electrovalent compound, whereas many acids in the pure state do not conduct, and are covalent compounds. Thus, hydrogen chloride in the liquid state, or in the state of dry gas, is covalent. Now water is both a donor and an acceptor (p. 162). The oxygen can act as donor, and the hydrogen as acceptor. The oxygen gives two electrons to the hydrogen of the hydrogen chloride,

which is then capable of ionisation, the hydrogen ion, however, being hydrated :—



It is obvious, too, that the hydrogen ion will be a more powerful acceptor than the hydrogen atom, and hence it will tend to co-ordinate with water, since the hydrogen atom itself will act as an acceptor in the association of water.

It is also to be noted that many acids in the anhydrous state possess a great affinity for water, *e.g.*, sulphuric acid. This may be due to the ease with which the hydrogen ion can be solvated.

There are thus several reasons for believing that the hydrogen ion does not exist in aqueous solutions unaccompanied by an atmosphere of water, which it carries with it. What we have previously said about the strength of an acid being due to the concentration of hydrogen ions in the solution, is, therefore, not quite correct, for the ions are hydrated. Actually, the solution of a strong monobasic acid in water is represented by the equilibrium

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-.$$

Wherever hydrogen ion concentration in aqueous solution is referred to, it must be understood that the H_3O^+ ion concentration is meant. As it is customary to use the term "hydrogen ion concentration," this nomenclature will be adhered to, although it is more accurate to write "hydroxonium ion concentration."

Although the initial work on strengths of acids indicated that it was largely the presence of the hydrogen ion that accounted for acidic properties, more recent work seems to show that the undissociated molecule itself, as well as the anions and hydrogen ions, hydrated or otherwise, must be considered as partly responsible for them. It was largely owing to the work of Arrhenius that the hydrogen ion view was put forward. As has already been stated, he showed that the order given by thermochemical and other methods, which were considered to indicate the strength of an acid, agreed with the order of their conductivity. From this it was argued that the concentration of hydrogen ions was the important thing in this connection. In 1890 Arrhenius carried out some experiments on the rate of inversion of cane-sugar by weak acids in the presence of their salts, and the results supported the hydrogen ion theory completely. Nine years later, however, Arrhenius found that the rate of inversion of cane-sugar was greatly increased if the neutral salt of a strong acid were added. The only way in which he could

explain this observation was to suppose that the dissociation constants of the acids were in some way increased by the presence of the neutral salts. This view was accepted for some time, during which it was shown that the undissociated molecule might be catalytically active ; in some cases even more so than the hydrogen ion itself. So the "dual theory" of acid catalysis originated, which argued that both the undissociated molecule and the hydrogen ions were active. The evidence for this was largely supplied by Goldschmidt, who showed that even in the presence of enough salt to reduce the ionisation of the acid practically to zero there is still a measurable catalytic effect. We can, therefore, say that the catalytic effect is shown by hydrogen ions, anions, undissociated molecules of weak acids, and by water molecules themselves, and it has also been shown that hydroxyl ions will catalyse the reaction. Thus, all substances, on the new definitions (§ 291), which are capable of acting as acids or as bases will catalyse the inversion of cane-sugar and many other organic reactions.

This can, in part, be explained by considering the reaction mechanism of this type of catalysis. This has been done in the case of the iodination of acetone by Dawson and his collaborators. The acetone is supposed first to combine with hydrogen ions giving an enolic substance, which splits off a hydrogen ion and becomes the enolic form of acetone. This is unsaturated, and can obviously react very readily with iodine.

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + H^+ \rightarrow \left[CH_3{-}\underset{\underset{OH}{|}}{C}{-}CH_3\right]^+ \rightarrow CH_3{-}\underset{\underset{OH}{|}}{C}{=}CH_2 + H^+$$

It is clear that what is wanted to catalyse this reaction is something that can supply and remove hydrogen ions, *i.e.*, an acid and a base. In aqueous solutions of acids it is thought that the water acts as the necessary base.

This view is also supported by the work of Lowry on the mutarotation of glucose in non-aqueous solutions. α-glucose itself is insoluble in organic liquids, and so tetramethyl glucose was used instead. In pyridine, a base, or in cresol, an acid, the rate of mutarotation was very much less than in water, but in a mixture of the two solvents the mutarotation was much greater than in water. Obviously, then, both base and acid were needed.

If the strength of an acid is to be measured by its catalytic effect, it is obvious, since the hydrogen ions themselves are not the only active catalytic agents, that the strength of the acid cannot be based on hydrogen ion concentration alone.

Confirmation of this view has come from rather unexpected

sources. As far back as 1902 it had been suggested by Kahlenberg that the corrosive power of acids as regards metals might depend upon the undissociated acid molecules as well as upon hydrogen ions. This view was arrived at from experiments on the solution of metals in hydrogen chloride in benzene. Recently Brønsted and Ross Kane found the rate of solution of sodium amalgam in solutions buffered with a weak acid and one of its salts, so that the p_H of the solution remained constant. It was found that although the hydrogen ion concentration remained constant on dilution, the rate of reaction decreased with decrease in concentration of undissociated acid. It seems therefore that the sodium atom reacts directly with the undissociated acid molecule.

The effect of this work on the definition of the strength of an acid will depend upon what view is taken of the definition. If the strength of an acid is defined as being proportional to the apparent hydrogen ion concentration in its solution, or to the dissociation constant K, the new work cannot affect the question. What has been shown is that typical acidic properties, such as corrosive power and catalytic activity, depend not only upon hydrogen ion concentration, but are complex functions of the concentrations of many molecular species. If, therefore, the term "strength" is adequately to cover acidic properties, the definition needs to be extended.

295. The Action of Water on Acids.—Many acids lose their acidic properties in the anhydrous state. It will be remembered that statements such as the following about hydrochloric acid gas frequently appear in text-books of inorganic chemistry: "The liquid gas will not turn litmus paper red, and will not combine with ammonia. Also, it will not dissolve calcium carbonate." Obviously, then, the presence of water makes a great deal of difference to the properties of an acid.

In some cases the reactions of acids are entirely altered according to whether there is water present or not. Thus nitric acid acts as a nitrating agent in the absence of water, or the presence of small quantities of water, tending to break up as shown :—

$$HNO_3 \longrightarrow OH + NO_2.$$

Substances, such as an aromatic hydrocarbon, which can supply hydrogen with which the OH group can combine to form water, are readily acted upon, and nitro-derivatives formed.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

If much water is present, however, this reaction is not observed,[1] and,

[1] A few aromatic substances, such as phenol, are nitrated by comparatively dilute nitric acid (1 : 3). This seems to point to incomplete dissociation into ions at this concentration.

instead, ionisation occurs, and the acid acts as a salt-producing substance, this property being masked, however, to a certain extent by its oxidising powers.

Very much the same thing is observed with strong sulphuric acid, which acts as a sulphonating agent when a suitable substance containing hydrogen is presented to it.

$$H_2SO_4 \longrightarrow HSO_3 + OH.$$

The acid in this case tends to form water. Thus, with benzene, benzene sulphonic acid is produced :—

$$C_6H_6 + H_2SO_4 = C_6H_5HSO_3 + H_2O.$$

With much water, however, ionisation occurs, and the acid no longer acts as a sulphonating agent.

Nitrous acid also shows the power to split off a OH group, particularly in organic reactions, when nitroso compounds are formed.

Perchloric acid shows a remarkable change in properties when water is added to it. Anhydrous perchloric acid is a substance that is difficult to handle, because it is such a powerful oxidising agent, and is liable to spontaneous explosion. When water is added, however, it becomes perfectly safe, and is, in fact, difficult to reduce. Metals will liberate hydrogen from dilute perchloric acid in the cold. The acid is completely dissociated in aqueous solution, and may be regarded as the strongest of acids, since its salts are very rarely hydrolysed in aqueous solution. Thus, it is possible to obtain aluminium perchlorate from solution by evaporation, whereas this method fails even for aluminium chloride.

These examples are sufficient to show that water exerts a remarkable influence in determining acidic properties, and it may be said that this effect is due to the ionisation brought about by the addition of water.

296. The Effect of the Solvent on the Properties of the Solute.—The acidity or alkalinity of a substance will obviously depend upon the nature of the solvent. Ordinary inorganic chemistry is so frequently the study of the properties of substances in contact with water that it is forgotten that these properties may be considerably altered in any other medium. Thus, a substance is classified as a base ; it may behave quite differently in another solvent. Thus, a basic solvent is a good ionising solvent for a weak acid, because the base itself tends to combine with hydrogen ions. Acetic acid, although weak in water, is a strong acid in liquid ammonia. On the other hand, an acidic solvent is a good ionising solvent for a weak base. Conant and Hall showed that benzamide, which is such a weak base in aqueous solution that the hydroxyl ion concentration

could not be measured, is quite a strong base in glacial acetic acid, in which it could actually be titrated potentiometrically with perchloric acid. A study of anhydrous formic acid as a solvent led Hammett and Dietz to a similar conclusion as regards urea. It is an exceedingly weak base in aqueous solution, its salts being almost completely hydrolysed, and yet it is a strong base in anhydrous formic acid.

Another striking result is that nitric acid, regarded as the strongest acid in aqueous solution, is a weak acid in methyl alcohol or ethyl alcohol (Hartley and Murray-Rust).

297. Liquid Ammonia as a Solvent.—Ammonia is a donor molecule

$$\begin{array}{c} H \\ \times\cdot \\ :N \overset{\times}{\cdot} H \\ \cdot\times \\ H \end{array}$$

It might therefore be expected to behave to a certain extent like water. Experiments on ammonia as a solvent show that in many ways it does behave like water. It is an ionising solvent, a property it owes largely to its fairly high dielectric constant (22). Liquid ammonia in the complete absence of water is a very poor conductor, just as water is in the absence of salts. It does, however, conduct a little, and the ions present must be NH_4^+ and NH_2^-, which have been formed by the dissociation of an ammonia molecule into a hydrogen ion and an NH_2^- ion, and the combination of the hydrogen with another NH_3 molecule. This corresponds to the case of water where the two ions are H^+ and OH^-, but the hydrogen ion attaches itself to water and forms the H_3O^+ ion. There are many other points in which ammonia resembles water. It has a high specific heat, it is an associated liquid, and it forms molecular complexes analogous to the hydrates.

Many salts will dissolve in liquid ammonia, and the solution is then found to be conducting. Indeed, the conductivity of a salt solution in liquid ammonia is usually greater than that of an aqueous solution of the same salt. This is due to the lower viscosity of the liquid ammonia. Certain substances may be classified into "ammono-acids," and "ammono-bases" on analogy with aqueous solutions. The dissociation of liquid ammonia takes place according to the equation

$$NH_3 \longrightarrow NH_2^- + H^+ \left(\begin{array}{l} + NH_3 \\ \longrightarrow NH_4^+ \end{array}\right).$$

Compare this with water

$$H_2O \longrightarrow OH^- + H^+ \left(\begin{array}{l} + H_2O \\ \longrightarrow H_3O^+ \end{array}\right),$$

and we see that the basic ion is the NH_2^- and the acidic ion NH_4^+. An ammono-acid is one which gives NH_4^+ ions in liquid ammonia solution, whilst an ammono-base is one which gives NH_2^- ions in liquid ammonia. The dissociation of liquid ammonia is small, and so an ammono-acid and an ammono-base cannot exist together in liquid ammonia solution, for they will combine to give the more or less undissociated ammonia. This is strictly analogous to the neutralisation of an acid by a base in aqueous solution. To give an example, an ammono-base is sodamide, whilst an ammono-acid is acetamide. These two will neutralise each other in liquid ammonia solution as follows :—

$$CH_3CONH.H + NaNH_2 = CH_3CO.NHNa + NH_3,$$

or, ionically,

$$(H^+ + NH_3) + NH_2^- \longrightarrow 2NH_3.$$

A process similar to hydrolysis in the case of aqueous solutions occurs with solutions in liquid ammonia, and may be referred to as "ammonolysis." Thus, mercuric chloride, dissolved in liquid ammonia, gives the compound $HgCl.NH_2$ and hydrochloric acid.

$$HgCl_2 + NH_3 \rightleftharpoons HgCl.NH_2 + HCl.$$

This serves to emphasise the fact that our chemistry is almost entirely aquo-chemistry—the chemistry of substances in aqueous solution, or in the presence of water. It is surprising what great differences in behaviour are found when other substances are used as solvents.

298. Amphoteric Electrolytes, or Ampholytes.—An amphoteric substance is one which behaves either as an acid or as a base, according to the circumstances. In other words, it can either supply or take up protons.

Many inorganic substances are amphoteric. Common examples are zinc hydroxide, $Zn(OH)_2$, aluminium hydroxide, $Al(OH)_3$, and stannous hydroxide, $Sn(OH)_2$. These amphoteric hydroxides are capable of forming salts with both acids and bases. Thus, zinc hydroxide combines with dilute sulphuric acid to give zinc sulphate, which gives a metallic cation. It also dissolves in sodium hydroxide solution, giving sodium zincate, Na_2ZnO_2, in which the metal is to be found in the anion. It is to be supposed that, although the ionisation of zinc hydroxide is very small, it can take place in two ways, according to the circumstances. Thus, it may give zinc and hydroxyl ions

$$Zn(OH)_2 \rightleftharpoons Zn^{++} + 2(OH)^-;$$

or it may give hydrogen ions and zincate ions

$$Zn(OH)_2 \rightleftharpoons 2H^+ + (ZnO_2)^{--}.$$

Suppose an alkali is added to a suspension of zinc hydroxide in

water. In this case, it is obvious that the second type of ionisation will be favoured, since hydrogen ions will be removed from the sphere of action by combination with hydroxyl ions to form water. Thus, the formation of zincate ions will proceed almost to completion. If, however, an acid is added to the suspension of zinc hydroxide in water, the first type of ionisation will be favoured, as hydroxyl ions will be removed by the added hydrogen ions. In the amphoteric hydroxides, it is really the hydroxyl group which is capable of ionising in two ways.

Many organic substances are also amphoteric, but here the amphoteric nature is due to a different cause. Organic ampholytes contain two different groups, one being acidic and the other basic in nature. The most common example of such a compound is an amino-acid, such as glycine (amino-acetic acid), $CH_2NH_2.COOH$. The $—NH_2$ group has basic powers, the —COOH group has acidic powers. The substance can, therefore, ionise in two ways in aqueous solution.

$$(1)\ NH_2.CH_2.COOH + H_2O \rightleftharpoons \overset{+}{N}H_3.CH_2.COOH + OH^-$$
$$(2)\ NH_2.CH_2.COOH \rightleftharpoons NH_2.CH_2.COO^- + H^+.$$

In the presence of an acid, the first type of ionisation will occur, the hydroxyl ions being removed by the added hydrogen ions. In the presence of an alkali, the second equation will express the ionisation, for the added hydroxyl ions will combine with hydrogen ions, and will tend to repress the formation of hydroxyl ions according to the first equation. Glycine forms both a hydrochloride and a sodium salt.

In the case of organic ampholytes, a third type of ion, which carries both a positive and a negative charge, can exist. These are known as "*Zwitter*" [1] or "dual" ions. Thus, glycine can produce the *Zwitter*-ion $\left[\overset{+}{N}H_3.CH_2.CO\overset{-}{O}\right]$.

$$NH_2.CH_2.COOH \rightleftharpoons \left[\overset{+}{N}H_3.CH_2.CO\overset{-}{O}\right].$$

It is probable that in aqueous solution an amino-acid exists almost entirely in the form of the Zwitter-ion. The addition of an acid converts the Zwitter-ion into the basic ion $[\overset{+}{N}H_3.CH_2.COOH]$,

$$\left[\overset{+}{N}H_3:CH_2.CO\overset{-}{O}\right] + H^+ \rightleftharpoons \left[\overset{+}{N}H_3.CH_2.COOH\right].$$

The removal of the Zwitter-ion results in further dissociation, and the acid further dissolves. The addition of a base converts the Zwitter-ion into the acidic ion $[NH_2.CH_2.COO]^-$,

[1] German "*Zwitter*" = hybrid.

$$\left[\overset{+}{N}H_3.CH_2.CO\bar{O}\right] + OH^- \rightleftharpoons \left[NH_2.CH_2.COO\right]^- + H_2O,$$

or $$[HO.NH_3.CH_2.COO]^-.$$

This can be compared with the action of acids and bases on ammonium acetate. If a strong acid is added to ammonium acetate, acetic acid is produced, together with ammonium ions ; if a base is added, acetate ions and ammonia molecules are formed. In an amino-acid, of formula $NH_2.R.COOH$, the ions are thus $\left[\overset{+}{N}H_3.R.COOH\right]$ and $[NH_2.R.COO]^-$, together with the Zwitter-ion $\left[\overset{+}{N}H_3.R.CO\bar{O}\right]$. The equilibria in the solution of the acid will be :—

$$\left[\overset{+}{N}H_3.R.COOH\right] \rightleftharpoons \left[\overset{+}{N}H_3.R.CO\bar{O}\right] + H^+,$$

and $$\left[NH_2.R.CO\bar{O}\right] + H_2O \rightleftharpoons [NH_3(OH).R.COO]^- \rightleftharpoons \left[\overset{+}{N}H_3.R.CO\bar{O}\right] + OH^-.$$

Since the amino-acid is capable of removing both $[H^+]$ and $[OH^-]$ ions, it will form a good buffer (§ 284). The proteins consist of complex amino-acids, and there is little doubt that the constant p_H value of the protein-containing liquids of the body, such as the blood, is due to this buffer action.

299. Double Salts and Complex Salts.—When solutions of two different salts are mixed in equivalent proportions, and the mixture is evaporated, it sometimes happens that the crystals forming are composed of a double salt. Thus, if solutions of equivalent quantities of ferrous sulphate and of ammonium sulphate are mixed, and the solution is evaporated, there separates out as a crystalline phase, ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$. This salt is somewhat different in appearance and properties from the salts from which it was made.

If silver cyanide is added to potassium cyanide solution, it dissolves, and from the solution a new salt, potassium argento-cyanide, $KAg(CN)_2$, is formed. This has notably different properties from either of the original salts. In solution there is no trace of silver ions detectable by chemical tests, but instead a complex ion, $(Ag(CN)_2)^-$, exists, together with potassium ions. There are a very large number of salts such as this, which are called "complex salts."

Examples of common complex salts are the ferro- and ferri-cyanides. The salts formed when silver chloride dissolves in ammonia, or in sodium thiosulphate, or in potassium cyanide, just mentioned, are complex salts.

There appears to be no definite line of demarcation between double salts and complex salts as far as chemical properties go. They are the extremes of a series of varying degrees of chemical combination. The differences lie only in the degree of stability of the complex ion. In what are usually called double salts, the complex ion is readily broken down into its constituents. Some authors (*e.g.*, Ephraim, *Inorganic Chemistry*, trans. P. C. L. Thorne) regard the schönites ($M^{II}SO_4.M^{I}_2SO_4.6H_2O$), of which ferrous ammonium sulphate is one, as complex salts ($M^{I}_2[M^{II}(SO_4)_2]^{II}.6H_2O$). The alums likewise they take to be not $M^{I}_2SO_4.M^{III}_2(SO_4)_3.24H_2O$, but $M^{I}[M^{III}(SO_4)_2].12H_2O$. This view regards all the double salts merely as very unstable complex compounds. An $[M^{II}(SO_4)_2]^{--}$ ion probably exists in a solution of ferrous ammonium sulphate, and there would only have to be a small amount of dissociation into M^{++} and $(SO_4)^{--}$ ions for these latter to be detected. As soon as they were removed from the solution by precipitation, more of the complex ion would decompose, giving, finally, complete breakdown of the complex ion.

Investigation of Complex Ions.—As a rule, complex salts are quite stable in the solid state, and *X*-ray analysis of their structure reveals the presence of the complex ion. There are, however, many ways in which the presence of complex ions in solution may be recognised. The chief of these are:—

(1) *Qualitative Analysis.*—It has already been stated that the complex salt ionises in a different way from a double salt. Although it contains two metals, one of them is to be found in the anion, and therefore is not evident in solution as a metal ion. Hence, the solution will not answer to the tests for that ion. Thus, if copper sulphate is treated with potassium cyanide a white precipitate of cuprous cyanide, $Cu_2(CN)_2$, is first produced, which dissolves in excess of the cyanide, giving a solution containing potassium cupro-cyanide, $K_2Cu(CN)_3$. This solution gives none of the tests for copper. Thus we find that if ammonium sulphide solution be added no black precipitate results. This fact is made use of in qualitative analysis in the separation of cadmium from copper. If to a solution containing both metals an excess of potassium cyanide is added, both metals form complex cyanides, but the cadmium compound is much less stable than the copper salt. Hence, addition of ammonium sulphide, or passage of hydrogen sulphide, precipitates the cadmium sulphide, but leaves the copper in the solution. The complex cadmium cyanide ion breaks down as follows:—

$$Cd(CN)_4^{--} \rightleftharpoons Cd^{++} + 4CN^-.$$

There is an equilibrium between these ions, and removal of Cd^{++} by ammonium sulphide results in the shifting of the equilibrium to the right, and so, finally, all the cadmium is precipitated. It is clear that only the most stable complex ions will fail to give the qualitative tests for their components.

The "transition" elements in the Periodic Table, together with the metals copper, silver and mercury, are all noted for the formation of complex ions. The electronic theory provides an explanation of this.

(2) *Solubility Method.*—If an inorganic substance is sparingly soluble in water, but very soluble in some aqueous solution, it is very likely that complex ion formation has taken place. The solubility is easily explained. Consider as before silver cyanide. This salt is very sparingly soluble in water. It may be supposed, however, to give a few silver and cyanide ions :—

$$AgCN \rightleftharpoons Ag^{+} + CN^{-}.$$

Addition of potassium cyanide should, on the theory of the solubility product (§ 288), depress the ionisation, and hence result in the precipitation of silver cyanide. What happens is, however, that the cyanide ion is removed as well as the silver ion in the formation of the complex $[Ag(CN)_2]^{-}$, and hence the equilibrium is destroyed and the silver cyanide goes into solution. Actually, although so much silver cyanide dissolves, there is a decrease in the silver ion concentration.

(3) *Distribution Method.*—According to the Distribution Law, the equilibrium in two phases between which a substance distributes itself exists only between molecular species which are identical. This fact is frequently applied to the study of the equilibrium between the halides and the halogens. Thus, the solution of bromine in potassium bromide has been investigated by Roloff by this method. Solutions of potassium bromide were shaken with strong solutions of bromine in carbon disulphide. The bromine distributed itself between the bromide layer and the disulphide layer. The amount present in each was determined by volumetric analysis. The distribution of bromine between water and carbon disulphide was also found.

Suppose that on shaking water with a solution of bromine in carbon disulphide a gram-molecules of bromine pass into the aqueous layer per litre. When shaken with a solution of KBr containing b gram-molecules per litre, then c gram-molecules of bromine pass into the aqueous layer. Then $c - a$ gram-molecules of bromine must have been used up in forming complex ions.

Suppose that the equilibrium is represented by

$$\begin{array}{ccccc} Br^- & + & Br_2 & \rightleftharpoons & Br_3^- \\ \{b-(c-a)\} & & a & & c-a. \end{array}$$

If the concentrations are as indicated in italics above, by the Law of Mass Action

$$K = \frac{(b-c+a)a}{c-a}.$$

Actually, Roloff found that K came out to be constant within the limits of experimental error, and so the above equation may be regarded as the correct one for expressing this equilibrium.

(4) *Ionic Migration Method.*—It is clear that the size of the ion and its nature will influence transport experiments (§ 260). Thus in a transport experiment it would be possible to indicate the presence of complex ions, and this was done by Hittorf for potassium ferrocyanide. His results are interesting, and should be read in connection with this work in the chapter on Electrolysis (§ 261).

13·7207 Gms. of solution before electrolysis gave, when evaporated with sulphuric acid and ignited, 2·0505 gms. of potassium sulphate, and 0·4869 gm. of ferric oxide. After electrolysis 23·3087 gms. of solution from the anode compartment gave 3·2445 gms. of potassium sulphate, and 0·8586 gm. of ferric oxide. The amount of current flowing was shown by a silver voltameter. During the experiment 0·5625 gm. of silver was deposited. The analysis quoted shows that the anode solution after electrolysis contained 1·4585 gms. of potassium and 0·60096 gm. of iron. In potassium ferrocyanide 1·4585 gms. of potassium is equivalent to 0·5281 gm. of iron. The excess of iron in the anode chamber is therefore 0·07286 gm. = 0·002602 equivalent. The silver deposited is 0·00521 equivalent. Hence, the valency of an ion containing one equivalent of iron is 0·00521/0·002602, or the valency of the complex ion containing 1 atom of iron is twice this, *i.e.*, 4.

(5) *Electromotive Force Measurements.*—The use of this method is described on p. 551.

(6) *Conductivity.*—This method was used largely by Werner in his study of co-ordination compounds.

The formation of complex compounds alters the number of ions present. Thus chromic chloride, $CrCl_3$, should give four ions, but actually it gives only two, owing to the formation of the co-ordination compound $[Cr(H_2O)_4Cl_2]Cl$. The conductivity is, therefore, proportionately diminished. The size of the ion also alters its mobility and therefore affects the conductivity of the solution.

(7) *Determination of Molecular Weight.*—It is known that the molecular weight of a substance in solution, as determined by any

of the colligative property methods, is dependent upon the number of individual particles present. Thus, when hydrogen iodide is added to iodine solution, it is found that the freezing point of the latter is unchanged. Hence, there cannot have been any alteration in the number of individuals in the solution. Thus the only possible changes are $I_2 + I^- \rightleftharpoons I_3^-$ or $2I_2 + I^- \rightleftharpoons I_5^-$, but not $I_2 + 2I^- \rightleftharpoons I_4^{--}$ or $I_2 + 3I^- \rightleftharpoons I_5^{---}$. In this way the number of possible complexes is limited.

SUMMARY

An acid is a compound containing hydrogen which can yield hydrogen ions (free or solvated) on solution in water; a base is a substance that will combine with hydrogen ions. The basicity of an acid is the number of hydrogen ions that can be formed from one molecule of the acid. The basicity of an acid can be determined (*a*) by finding the number of true salts it can form with sodium hydroxide; (*b*) by direct titration; (*c*) by finding the amount of heat evolved when one gram-molecule of the acid is treated with one gram-molecule, or integral multiples of one gram-molecule of sodium hydroxide; (*d*) by using Ostwald's empirical conductivity rule that $\Lambda_{32} - \Lambda_{1024} = 10\,n$, where n is the basicity of the acid.

The strength of an acid is not measured by its corroding power. The strength of an acid is defined as being proportional to the hydrogen ion concentration of its solution, and is therefore measured by the dissociation constant K, but it is now known that the anion and the undissociated molecule also play some part in deciding the characteristic acidic properties. Hydrogen ion concentration is best determined by means of the hydrogen electrode. A cell is made, consisting of a hydrogen electrode in the solution of which the p_H is required, and a calomel electrode of known potential, the bridge solution being a saturated solution of potassium chloride. The e.m.f. of the cell is measured, and the p_H calculated from a formula. Other methods are (*a*) conductivity determination, (*b*) freezing point method, (*c*) indicator method, (*d*) catalysis of ester hydrolysis.

The properties of acids are profoundly affected by the presence of water. Most acids in the pure state are covalent, but, on addition of water, become electrovalent. In general, the solvent exerts a decisive influence on the properties of the solute. This becomes obvious on considering solutions in liquid ammonia.

Besides the clear-cut acids and bases, there are also amphoteric electrolytes, such as zinc hydroxide, which act either as acids or bases according to the circumstances. Amphoteric organic substances are best represented by amino acids, which can not only ionise to give acidic or basic solutions, but can also give Zwitter-ions, which bear no resultant charge. Thus, the amino acid $CH_2NH_2.COOH$ can give $[\overset{+}{N}H_3.CH_2.CO\overset{-}{O}]$ (Zwitter-ion), $[\overset{+}{N}H_3.CH_2.COOH]$ (basic ion) and $[NH_2.CH_2.CO\overset{-}{O}]$ (acidic ion). Complex salts and double salts cannot be regarded as two distinct types of salt. Double salts are very unstable complex salts. Complex ions may be investigated and their presence

shown (*a*) by qualitative analysis, (*b*) by solubility, (*c*) by distribution methods, (*d*) by ionic migration, (*e*) by e.m.f. measurements, (*f*) by conductivity measurements, and (*g*) by depression of freezing point.

QUESTIONS

(1) How far is it true to say that the strength of an acid is determined by the hydrogen ion concentration of its solution ?

(2) By what methods may hydrogen ion concentration be determined? Indicate the importance of hydrogen ion concentration values.

(3) Show by examples the effect of addition of water on the properties of an acid.

(4) Define the terms "acid" and "base." Criticise the usually accepted definitions.

(5) "An acid is a substance that turns blue litmus red." Is this, in your opinion, a good and sufficient definition of an acid ?

CHAPTER XV

THERMOCHEMISTRY

300. General.—Whenever any chemical reaction takes place, heat is either absorbed or evolved. This is due to the fact that chemical compounds have various amounts of energy associated with them, and as the energy of the products of a reaction is never equal to that of the reactants, heat is evolved or absorbed when the reaction takes place.

Heat is measured in calories. It is a common error to confuse temperature with heat, but temperature is merely the level of heat, determining whether heat will flow from one body to another placed in thermal contact with it. The gram-calorie is the amount of heat required to raise the temperature of 1 gm. of water through 1° C. As this value varies slightly with temperature, it is customary, for accurate work, to specify the temperature over which the gram-calorie is to be measured. As a rule, the degree specified is 14°–15° C., though other figures have been proposed.

Since the amount of heat evolved and absorbed in any chemical reaction taking place between the weights of substances represented by the formulæ in the equation is usually fairly large, and runs into thousands of gram-calories, it is sometimes convenient to use the kilogram-calorie, *i.e.*, the amount of heat required to raise the temperature of 1 kilogram of water through 1° C. It is one thousand times as large as the ordinary gram-calorie. The ordinary gram-calorie is written with a small " c " and the kilogram-calorie with a capital " C." The term " *heat tonality* " is sometimes used to denote the amount of heat associated with a chemical reaction.

301. Heat of Reaction.—The heat of reaction is defined as the number of gram-calories of heat *evolved* when the reaction takes place *at constant volume*, in the direction indicated by, and between, the amounts of substances shown in the equation. Thus, the equation

$$\underline{C} + \bar{O}_2 = \overline{CO}_2 + 94{,}380$$

means that when 12 gms. of solid carbon combine with 32 gms. of gaseous oxygen to form 44 gms. of gaseous carbon dioxide, 94.380 gm.-calories are evolved. It is necessary to specify the state

in which the reactants or products are employed, or obtained, since heat will be absorbed or liberated in changes of state (*e.g.*, from solid to liquid, or liquid to gas, or *vice versâ*). This is indicated in the equation by putting a bar over the substance if it is a gas and a bar under it if it is a solid, and nothing at all if it is a liquid. Heat evolved is given a positive sign, heat absorbed a negative sign.

The symbol *aq* in a thermochemical equation signifies that the

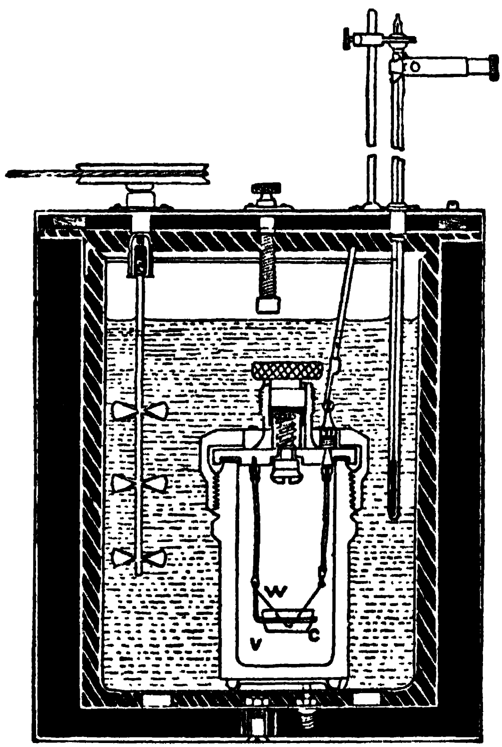


FIG. 187.—Berthelot's Bomb Calorimeter.

substance is present with plenty of water, sufficient in fact to make the addition of any further quantity of it have no effect on the heat evolved. In this condition its *heat of dilution* is negligibly small.

Reactions are frequently classified according to type for thermochemical purposes, and the heats evolved are given different names according to the type to which they belong. Thus there are heats of combustion, heats of formation, heats of neutralisation, heats of dilution, heats of dissociation, heats of atomisation, heats of precipi-

tation, etc. They are all, however (with the possible exception of heat of dilution) heats of reaction.

302. Heat of Combustion.—The heat of combustion of a compound or element is *the amount of heat evolved when one gram-molecule of it is burned in oxygen at constant volume.* Thus

$$\underline{C_{12}H_{22}O_{11}} + 12\bar{O}_2 = 12\overline{CO}_2 + 11\overline{H_2O} + 1{,}243{,}000.$$

This means that when one gram-molecule of cane-sugar is burnt in excess of oxygen, 1,243,000 gm.-calories of heat are given out.

The heat of combustion is determined experimentally by means of Berthelot's Bomb Calorimeter. The general form of this apparatus is shown in Fig. 187.

The apparatus consists of a very strong vessel (V) and cover, made of steel, nickelled on the outside, and coated on the inside with some non-oxidisable material, such as gold, platinum or enamel. The cover is fitted to the vessel by a piece of metal screwed to the body of the bomb. Through the centre of the cover is an inlet tube and valve, through which oxygen can be passed. There is a platinum wire W connected to a platinum cup C, and another platinum wire which passes through an insulating washer in the cover. The purpose of this is to enable an electric current to be passed to start the combustion.

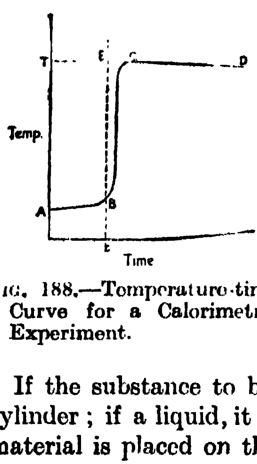


FIG. 188.—Temperature-time Curve for a Calorimetric Experiment.

If the substance to be burnt is a solid, it is compressed into a cylinder ; if a liquid, it is placed in the platinum capsule (C). The material is placed on the platinum support, and above it the two platinum wires W are joined by a thin spiral of iron wire. The bomb is closed and oxygen introduced through the inlet tube until there is a pressure of about 25 atmospheres inside. The screw valve is then tightened, and the bomb is immersed in water placed in a calorimeter. The temperature of the water is taken, and then the combustion is started. The temperature is then read every minute, and the results plotted. A curve like that shown in Fig. 188 is obtained. By extrapolating, the maximum temperature attained during the combustion is derived. The portion AB represents the variation of temperature of the calorimeter and contents with time before the reaction begins. At time t the reaction starts, and the curve now takes the course BCD, CD representing the cooling with time. To obtain the maximum temperature actually reached during the reaction, draw a perpendicular BE through B, and produce CD

backwards to cut it at E. The temperature T corresponding to this is the temperature required. For the calculation it is necessary to know the water equivalents of all the instruments used.[1] These have to be determined previously by immersing the instrument in water at a known temperature, and noting the decrease in temperature. The heat due to the combustion of the iron wire must be subtracted from the final result.

* **303. Heat of Formation. Intrinsic Energies.**—The heat of formation is defined as *the heat evolved when one gram-molecule of a substance is formed from its elements at constant volume.*

It is usually difficult to obtain the heat of formation of a compound directly, except where it is an oxide, and then the heat of formation coincides with the heat of combustion. Thus, it is not possible to make sodium hydroxide directly from its elements. In cases of this kind it is necessary to derive the heat of formation from the heat evolved in a number of other reactions, making use of Hess's Law (§ 304).

The heat of formation of a compound is an important constant for that compound. As will be seen later, it decides the stability of the molecule. The heat of formation will also give us information as to the amount of energy contained in a molecule. Thus, the heat of formation of methane is about 18,800 gm.-cals. This means that

$$\underline{C} + 2\ddot{H}_2 = \overline{CH}_4 + 18{,}800.$$

Since, by the law of conservation of energy, the energy liberated in the form of heat cannot have come from nowhere, the elements carbon and hydrogen, from which the methane was made, must have altogether 18,800 gm.-cals. more energy than the methane molecule. The methane itself must have 18,800 gm.-cals. less energy than the elements from which it was made, *i.e.*, $-18{,}800$ gm.-cals. more. This amount of energy associated with a compound is called its relative *intrinsic energy*. It is equal to the heat of formation of the compound with its sign changed. Since we are not yet fully acquainted with the intrinsic energies of elements, they are all placed arbitrarily at zero. We know this cannot be correct ; it is highly unlikely that the energy content of all atoms should be the same. But our knowledge of the value of this intrinsic energy is not certain, so at the moment it is necessary for us to base our practical definition on the older view that all elements have the same intrinsic energy, and this is placed arbitrarily at zero. The subject will be further discussed later (§ 310).

[1] The water equivalent is the mass of water which would require the same quantity of heat to raise its temperature through 1° C. as is required by the instruments (calorimeter, thermometer, etc.) for this purpose.

This convention makes it very easy to calculate heats of formation, etc. Thus, we see that the intrinsic energy of a compound is its heat of formation with the sign reversed. The intrinsic energy of 1 gm.-molecule of methane is $-18,800$ gm.-cals. The point to remember is that the sum of the energies on both sides of a thermochemical equation must be the same, in order to satisfy the law of conservation of energy.

An example of the use of this conception in the calculation of heats of formation may be given. From the heats of formation of carbon dioxide from carbon and from carbon monoxide respectively

$$\underline{C} + \bar{O}_2 = \overline{CO}_2 + 97,650 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\overline{CO} + \tfrac{1}{2}\bar{O}_2 = \overline{CO}_2 + 68,000 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

it is required to calculate the heat of formation of carbon monoxide.

The equation for the heat of formation of CO is

$$\underline{C} + \tfrac{1}{2}\bar{O}_2 = \overline{CO} + x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where x is the heat of formation.

From equation (1) the intrinsic energy of carbon dioxide is

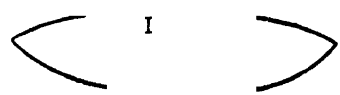


FIG. 189.

$-97,650$ cals. From equation (3) that of CO is $-x$. Writing the values of the intrinsic energies in equation (2), we have

$$-x - 0 = -97,650 + 68,000.$$

Hence, $\qquad x = 29,650$ cals.

304. Hess's Law of Heat Summation.—*If a chemical change can be made to take place in two or more different ways, then the amount of heat absorbed or evolved in the total change is the same no matter by which method the change is carried out.* This Law, which is merely a consequence of the First Law of Thermodynamics (Law of Conservation of Energy), was first stated by Hess in 1840. If the law were not true it would be possible to obtain energy without a corresponding expenditure of work, for suppose that, by taking the path AcB from A to B, a certain amount of heat is given out, whereas by going *viâ* AdB at the same temperature the amount of heat evolved is less than before. Then, by going *viâ* AcB, and returning *viâ* BdA, the amount of heat given out in the first minus that given out in the second would be available for external work.

The Law has been tested experimentally and found to be true. A good example is to calculate the heat of formation of a dilute solution of ammonium chloride from its elements. This can be done in two ways :—

(1) Prepare solid ammonium chloride from ammonia and hydrogen chloride. Then dissolve it in excess of water.

(2) Prepare a solution of ammonia and one of hydrogen chloride in equivalent amounts and mix the two. The amounts of heat evolved in these changes are given in the following equations :—

$$
\begin{array}{lrl}
\text{I.} & \overline{NH_3} + \overline{HCl} & = \overline{NH_4Cl} + 42{,}100. \\
 & \overline{NH_4Cl} + aq & = NH_4Claq - 3{,}900. \\
 & \therefore\ \overline{NH_3} + \overline{HCl} + aq & = NH_4Claq + 38{,}200. \\
\text{II.} & \overline{NH_3} + aq & = NH_3aq + 8{,}400. \\
 & \overline{HCl} + aq & = HClaq + 17{,}300. \\
 & HClaq + NH_3aq & = NH_4Claq + 12{,}300. \\
 & \therefore\ \overline{NH_3} + \overline{HCl} + aq & = NH_4Claq + 38{,}000.
\end{array}
$$

It is seen that the amount of heat evolved in the two methods is the same, within the limits of experimental error.

Hess's Law is of great practical importance, since it enables the heat of reaction to be calculated in cases where it cannot be measured directly. Thermochemical equations may be added or subtracted. Indeed, they may be regarded just as algebraical equations. In thermochemical calculations it is of the utmost importance to make certain of the sign of the heat (+ or —).

305. Exothermic and Endothermic Compounds.—Compounds which are formed with evolution of heat are called *exothermic compounds*. Those formed with absorption of heat are called *endothermic*. This fact about a compound is of very great importance, since it enables us to predict its stability. An endothermic compound will contain more energy than the substances from which it was made. If a compound is formed with absorption of heat, it follows from Le Chatelier's theorem (§ 138) that it will be stable at high temperatures. It will require high temperatures for its formation, since the absorption of heat tends to annul the constraint put on the system. Endothermic compounds are therefore not stable at low temperatures. They can be kept indefinitely at such temperatures by freezing the equilibrium (p. 343), but not otherwise.

Exothermic compounds will be stable at ordinary temperatures, but unstable at high temperatures, for a similar reason.

Among endothermic compounds are to be found the oxides of nitrogen, hydrogen iodide, ethylene, acetylene, ozone and hydrogen peroxide. These are all substances which are formed from their elements in appreciable quantities only at high temperatures.

TABLE CII.—HEATS OF FORMATION

Substance.	Heat of Formation, gm.-cals.
Hydrogen chloride (gas)	22,000
Hydrogen bromide (gas)	8,440
Hydrogen iodide (gas)	− 6,400
Hydrogen fluoride (gas)	38,500
Carbon dioxide (gas)	94,380
Ammonia (gas)	11,890
Nitrous oxide (gas)	− 20,600
Nitric oxide (gas)	− 21,600
Nitrogen trioxide (gas)	− 22,200
Nitrogen dioxide (gas)	− 3,000
Nitrogen pentoxide (solid)	− 30,000
Hydrogen sulphide (gas)	2,730
Ozone (gas)	− 34,000
Hydrogen peroxide (liq.)	− 23,000
Water (liq.)	68,380

* **306. Heat of Neutralisation.**—The heat of neutralisation of an acid by a base is defined as *the amount of heat evolved when one gram-equivalent of the acid is neutralised by a base.*

For strong acids and bases the value obtained is constant, and equal to about 13,700 gm.-cals (see Table XCIV, p. 556).

The reason for the constancy of the heat of neutralisation of a strong acid by a strong base is that the reaction is always merely the combination of hydrogen ions and hydroxyl ions to form undissociated water. Thus, when sodium hydroxide solution, of which the solute consists entirely of sodium ions and hydroxyl ions, is mixed with hydrochloric acid also consisting entirely of hydrogen ions and chloride ions and water, it forms sodium chloride, which can be regarded as completely ionised, and water. The reaction is therefore effectively the combination of hydrogen and hydroxyl ions.

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$$
$$OH^- + H^+ = H_2O.$$

The heat of neutralisation can be used to determine the basicity of an acid. For details of this see p. 587.

* **307. Determination of the Heat of Neutralisation.**—The calorimeter used for this work must, of course, be made of glass. It may consist of two beakers separated from each other by cloth, or some

other lagging material, or, better, it may be a vacuum flask. The latter makes a very efficient calorimeter.

In all calorimetric work it is necessary first of all to determine the water equivalent of the calorimeter and stirrer and thermometer. This is done by heating some water to the boiling point in a test-tube, taking its temperature, and then pouring it quickly into the calorimeter which has inside it the stirrer and thermometer to be used in the experiment. The temperature of the calorimeter may be taken as being the temperature of the room at the commencement of the determination. The temperature of the hot water in the calorimeter is taken every half minute, and the results plotted. A curve of the form shown in Fig. 188, p. 610, will be obtained. If a vacuum flask is used the portion BC will be very nearly horizontal, and this may be taken as the temperature attained by the flask. Otherwise it will be necessary to extrapolate the portion BC back to the temperature axis. This point will be the temperature which the calorimeter would have reached had there been no loss of heat due to radiation and conduction.

The water equivalent of the calorimeter is its mass multiplied by its specific heat, and is represented by W. Then, if t_1 was the temperature of the calorimeter before the hot water was added, t_2 its temperature afterwards, t_3 the temperature of the boiling water, and m the mass of the hot water, then the heat given out by the boiling water is $m(t_3 - t_2)$ gm.-cals. That taken in by the calorimeter is $W(t_2 - t_1)$ gm.-cals. These two amounts of heat must be equal.

$$W(t_2 - t_1) = m(t_3 - t_2).$$

This equation gives W. To determine m, the water from the calorimeter is poured into a weighed flask and weighed.

Take 50 c.c. of normal sodium hydroxide and note its temperature (t_4), and 50 c.c. of normal hydrochloric acid, and note its temperature (t_5). The two temperatures will usually be the same, but they need not be. Pour the two solutions into the calorimeter, and take the temperature every half minute, the liquid being stirred all the time. Plot a cooling curve and extrapolate as before. If m_1 is the mass of the salt solution, and s its specific heat, and t_6 the final temperature, then the initial temperature of the liquid was $(t_4 + t_5)/2$, and the amount of heat given out must have been

$$m_1 s\left(t_6 - \frac{t_4 + t_5}{2}\right) + W(t_6 - t_1).$$

The value of $m_1 s$ may be taken as 100, since the mass will be a little over 100 gms., and the specific heat a little less than 1. The error in doing this will be less than 1 per cent. The value obtained must

be multiplied by 20 to give the amount of heat evolved when 1 gm.-molecule of sodium hydroxide is neutralised by hydrochloric acid.

Similar apparatus and methods are employed for the determination of other heats of reaction.

308. Some Numerical Examples.—(1) From the heat of combustion of ethyl alcohol and acetic acid respectively

$$C_2H_5OH + 3\bar{O}_2 = 2\overline{CO}_2 + 3H_2O + 325{,}700 \quad . \quad . \quad . \quad (1)$$

$$CH_3COOH + 2\bar{O}_2 = 2\overline{CO}_2 + 2H_2O + 209{,}400 \quad . \quad . \quad . \quad (2)$$

calculate the heat of the reaction

$$C_2H_5OH + \bar{O}_2 = CH_3COOH + H_2O \quad . \quad . \quad . \quad . \quad (3)$$

This can be obtained merely by subtracting (2) from (1). We have

$$C_2H_5OH + \bar{O}_2 - CH_3COOH = H_2O + 116{,}300,$$

$$\therefore C_2H_5OH + \bar{O}_2 = CH_3COOH + H_2O + 116{,}300 \text{ gm.-cals.}$$

The heat of the reaction is 116,300 *gm.-cals.*

(2) Calculate the heat of formation of cane sugar from the data

$$C_{12}H_{22}O_{11} + 12\bar{O}_2 = 12\overline{CO}_2 + 11\overline{H_2O} + 1{,}243{,}000,$$

$$C + \bar{O}_2 = \overline{CO}_2 + 94{,}380,$$

$$2\bar{H}_2 + \bar{O}_2 = 2\overline{H_2O} + 136{,}760.$$

Let x be the heat of formation. Then $-x$ is the intrinsic energy. Substituting intrinsic energies in the first equation,

$$-x + 0 = 12(-94{,}380) + 11(-68{,}380) + 1{,}243{,}000,$$

$$= -1{,}132{,}560 - 752{,}180 + 1{,}243{,}000,$$

$$= -641{,}740.$$

$\therefore$ *The heat of formation is* 641,740 *gm.-cals.*

(3) Find the heat of formation of sodium hydroxide from the following data :—

$$Na + aq = NaOHaq + \tfrac{1}{2}H_2 + 98{,}000 \quad . \quad . \quad . \quad (1)$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68{,}380 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$NaOH + aq = NaOHaq + 13{,}300 \quad . \quad . \quad . \quad . \quad (3)$$

In equation (1) aq on the left-hand side includes the H_2O used up. The heat of the reaction

$$Na + H_2O = NaOH + \tfrac{1}{2}H_2 \text{ is first required.}$$

Rewriting (1),

$$Na + H_2O + aq = NaOHaq + \tfrac{1}{2}H_2 + 98{,}000.$$

Instead of NaOHaq we may write from (3), $NaOH + aq - 13{,}300$

$$Na + H_2O + aq = NaOH + aq + \tfrac{1}{2}H_2 + 84{,}700$$

$$\therefore Na + H_2O = NaOH + \tfrac{1}{2}H_2 + 84{,}700 \quad . \quad . \quad (4)$$

Let the heat of formation of NaOH be x. Its intrinsic energy $= -x$. Then substituting in (4)

$$0 - 68{,}380 = -x + 84{,}700.$$
$$\therefore x = 153{,}080 \text{ gm.-cals.}$$

The heat of formation is 153,080 *gm.-cals.*

(4) Deduce the heat of formation of benzene from the following data ?

$$C_6H_6 + 7\tfrac{1}{2}\bar{O}_2 = 6\overline{CO}_2 + 3\overline{H_2O} + 754{,}300 \quad . \quad . \quad (1)$$
$$\underline{C} + \bar{O}_2 = \overline{CO}_2 + 94{,}380 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$\bar{H}_2 + \tfrac{1}{2}\bar{O}_2 = \overline{H_2O} + 68{,}380 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let the required heat of formation be x. Substituting intrinsic energies in equation (1)

$$\begin{aligned} -x + 0 &= -566{,}280 - 205{,}140 + 754{,}300 \\ &= -771{,}420 + 754{,}300 \\ &= -17{,}120. \end{aligned}$$

The heat of formation of benzene is therefore 17,120 *gm.-cals.*

309. Correction of Thermochemical Data for Constant Pressure.—All heats of formation and combustion are obtained for a system at constant volume. If it is required to find the heat evolved at constant pressure, a correction must be applied. At constant volume the reaction performs no external work. If, however, the reaction takes place at constant pressure, and this causes an increase in volume of v, then external work is done to the extent of pv. This amount must be subtracted from the heat evolved at constant volume to obtain that at constant pressure. For liquids and solids the amount of the correction is small, since they undergo little expansion on heating under constant pressure ; but for gases it may be considerable, and must be calculated for each individual case from the data given.

310. Heats of Atomisation.—Modern research in thermochemistry centres round the determination of the heat evolved in the rupture or formation of the various possible linkages, such as the covalent link (§ 60), the semipolar double bond (§ 61), etc. We have previously taken the intrinsic energies of the elements as zero, but, strictly speaking, this is certainly untrue. Carbon in the form of diamond is a complicated structure of atoms joined together by certain bonds. When carbon dioxide is formed out of it, all these bonds have to be broken, and energy will be required for it. Similarly, the oxygen molecule has to be broken down to its atoms before it will combine with carbon to form carbon dioxide. Here again links have to be broken, and it is highly unlikely that the links

between the oxygen atoms will have the same energy content as those between the carbon atoms in the diamond. Hence, it is untrue to say that the intrinsic energies of these two elements are the same and can be placed arbitrarily at zero.

To discover the energy associated with the links which hold atoms together in molecules it is necessary to find the heat of atomisation of the elements. Where the element is a diatomic one, all that has to be done is to determine its heat of dissociation into atoms. This heat can be determined in several ways; though most of them, and particularly those which are generally applicable, depend upon a study of spectra, the theory of which we cannot consider here. Suffice it to say that these values have been determined and are collected together in the following Table:—

TABLE CIII.—HEATS OF ATOMISATION OF ELEMENTS [1]

(Figures are given in kg.-cals. per gm.-atom)

Element.	State.	Heat of Atomisation.
Hydrogen . . .	Gas	51·5
Oxygen . . .	Gas	59
Nitrogen . . .	Gas	104
Carbon . . .	Solid	150
Fluorine . . .	Gas	32·0
Chlorine . . .	Gas	28·7
Bromine . . .	Gas	24·9
	Liquid	28·7
Iodine. . . .	Gas	18·0
	Solid	25·5
Sulphur . . .	S_2 gas	52·0
	Rhombic	66·8

311. Heats of Formation of Linkages.—Knowing the following heats of combustion

$$\underline{C} + \overline{O}_2 = \overline{CO}_2 + 94{,}380,$$
$$\overline{H}_2 + \tfrac{1}{2}\overline{O}_2 = \overline{H_2O} + 68{,}380,$$

and one or two others, it is possible to calculate the heat of formation of many organic substances from their elements, since their heats of combustion are known. But this ordinary heat of formation from the elements, which we may call H_f, does not include the heat of atomisation of the elements. The heat of formation of the

[1] Taken, by permission, from Sidgwick's *Covalent Link in Chemistry* (Cornell University Press).

compound from its constituent atoms will therefore be given by H_f + the heats of atomisation of the elements.

Thus, for methane, the heat of combustion is 212·7 kg.-cals. Hence, its heat of formation is

$$H_f = -212{\cdot}7 + (94{\cdot}38 \times 1) + (34{\cdot}19 \times 4),$$
$$= +18{\cdot}5.$$

To obtain the atomic heat of formation, H_a, we must add the heats of atomisation of one C and four H = 150 + (4 × 51·5) = 356·0. Hence, H_a = 374·5 kg.-cals.

Now consider ethane, C_2H_6. Its heat of combustion is 368·3 kg.-cals. Hence,

$$H_f = -368{\cdot}3 + (2 \times 94{\cdot}38) + (6 \times 34{\cdot}19)$$
$$= +25{\cdot}6$$
$$H_a = 25{\cdot}6 + (2 \times 150) + (6 \times 51{\cdot}5)$$
$$= 634{\cdot}6 \text{ kg.-cals.}$$

From these two observations it is possible to calculate the heat of rupture of the C—H and the C—C links. We must assume that the heat of rupture is the same in both compounds.

Let x be the heat of rupture of the C—H link, and y that of the C—C link. Then, since methane contains four C—H linkages, presumably all the same, $4x = 374{\cdot}5$ and $x = 93{\cdot}6$ kg.-cals. Now in ethane we have six C—H linkages, and one C—C linkage. Hence, $6x + y = 634{\cdot}6$ and $y = 73{\cdot}0$ kg.-cals.

These values can be tested independently of a knowledge of heats of atomisation by considering the homologous paraffin series. If the energy associated with the linkages is the same in all the paraffins, then the heat of combustion, and the heat of formation from the elements H_f, and the heat of formation from the constituent atoms, will all differ by the same amount on passing from one member to the rest. This is found to be the case.

The heat of rupture of these linkages can be determined by other methods, mainly spectroscopic, and give results in good agreement with those obtained from thermochemical data.

When we treat other linkages in this way, and try to verify our conclusions by considering homologous series, the results are not so fortunate as with hydrocarbons. Thus, if we take the series of ketones, we find that the increase in the heat of formation for addition of CH_2 varies as the series is ascended. Hence, the value of the energy of the link must increase as the series is ascended. At present there is no satisfactory explanation of this, though several have been advanced. The heats of formation of various linkages are given in Table CIV.

TABLE CIV.—HEATS OF FORMATION OF LINKS

(In kilogram-calories.)

Link.	Heat.	Substances.	Link.	Heat.	Substances.
H – H	103·0	H_2 gas	C = S	130·9	Isothiocyanates
C – C	75·0	Diamond	C – Cl	75	Alkyl chlorides
[1] C_{al} – C_{al}	71·14	Paraffins	C – Br	62	Alkyl bromides
C_{al} – C_{ar}	79·40	Aromatic	C – I	45	Alkyl iodides
C_{ar} – C_{ar}	97·17	Aromatic	N ≡ N	208	N_2 gas
C = C	123	Olefines	N – H	89·8	Ammonia
C ≡ C	161	Acetylenes	N – N	87·0	Alkylamines
C_{al} – H	93·61	Paraffins	O = O	118	O_2 gas
C_{ar} – H	101·73	Aromatic	O – H	110	H_2O gas
C – N	60·0	Alkylamines	O – H	106	Alcohols
C = N	125·3	Isocyanates	S = S	104	S_2 gas
C ≡ N	183·0	Cyanogen	S – H	88·2	H_2S
C ≡ N	187·5	Acetonitrile	S – H	85	Mercaptans
C ≡ N	183	Isocyanides	Se – H	*ca* 66	H_2Se
C – O	76·5	Ethers	Te – H	*ca* 54	H_2Te
C – O	79·5	Acetals	F – F	64	F_2
C = O	160	Aldehydes	Cl – Cl	57·4	Cl_2
C = O	167	Ketones	Br – Br	49·8	Br_2 gas
C = O	182	Esters	I – I	36·0	I_2 gas
C = O	181·3	Carbon dioxide	F – H	147·6	HF
C ≡ O	235·5	Carbon monoxide	Cl – H	102·2	HCl
C – S	62	Alkyl sulphides	Br – H	86·7	HBr
C – S	59·3	Thiocyanates	I – H	70·9	HI
C = S	128·6	Carbon bisulphide	N – F	75·3	NF_3
N – Cl	59	Cl – N = O	Cl – F	88·1	ClF
N – O	64·2	Methyl nitrite	Cl – Br	52·8	ClBr
Cl – O	47·2	Cl_2O	Cl – I	47·6	ICl
N = O	125	Nitrous oxide	Br – I	42	IBr

(Taken, by permission, from Sidgwick's, *The Covalent Link in Chemistry*, Cornell University Press.)

SUMMARY

The heat of reaction is the number of gram-calories of heat evolved when the reaction takes place at constant volume, in the direction indicated by, and between the amounts of substances shown in, the equation.

The heat of combustion of a compound or element is the amount of heat evolved when one gram-molecule of it is burned in oxygen at constant volume. Heats of combustion are determined by means of Berthelot's Bomb Calorimeter.

The heat of formation is the heat evolved when one gram-molecule of a substance is formed from its elements at constant volume. The

[1] C_{al}, and C_{ar} stand for a carbon atom in an aliphatic and an aromatic compound respectively.

amount of energy contained in one gram-molecule in excess of that contained by its elements is called its "intrinsic energy," and is equal to the heat of formation with its sign changed, the intrinsic energies of the elements being taken arbitrarily as zero.

If a chemical change can be made to take place in two or more different ways, then the amount of heat absorbed or evolved in the total change is the same no matter by which method the change is carried out. (Hess's Law of Heat Summation.)

Compounds formed with evolution of heat are called "exothermic compounds." They are stable at low temperatures, but unstable at high temperatures. Compounds formed with absorption of heat are called "endothermic compounds." They are stable at high temperatures and unstable at low temperatures.

The heat of neutralisation of an acid by a base is the amount of heat evolved when one gram-equivalent of the acid is neutralised by a base. For a strong acid and a strong base, the heat of neutralisation is always 13,700 gm.-cals., since the ultimate reaction involved is always the same, *viz.*, $H^+ + OH^- = H_2O$.

All heats of formation and combustion are found at constant volume. A correction is necessary to obtain the values at constant pressure. It is now possible to derive the heat of atomisation of an element and the heat evolved or absorbed on breaking different linkages.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 38.—Determine the heat of neutralisation of (*a*) sodium hydroxide by hydrochloric acid, and (*b*) sodium hydroxide by acetic acid.

Experiment 39.—Determine the heat of solution of ammonium chloride.

Experiment 40.—Determine the heat of precipitation of silver chloride.

Experiment 41.—Determine the basicity of phosphoric acid. The method that can be applied for the performance of these experiments is described on p. 614. It will require but little modification to suit each experiment.

SUGGESTIONS FOR FURTHER READING

Sidgwick, N. V. "The Covalent Link in Chemistry," Chapter 4. (*Cornell University Press*, 1933.)

Thomsen, J. "Thermochemistry." (*Longmans.*)

QUESTIONS

√(1) What is meant by heat of formation and heat of combustion? Calculate the heat of formation of potassium hydroxide from the following data :—

$$\begin{aligned} K + H_2O + aq &= KOHaq + \tfrac{1}{2}H_2 + 48{,}000 \\ H_2 + \tfrac{1}{2}O_2 &= H_2O + 68{,}380 \\ KOH + aq &= KOHaq + 14{,}000 \end{aligned}$$

(2) What differences are to be noted between chemical compounds

according as they are formed with evolution or absorption of heat? Describe the commercial preparation of an endothermic gas.

(3) How can it be shown whether heat is absorbed or evolved in the dissociation of phosphorus pentachloride?

(4) Calculate the heat of formation of anhydrous aluminium chloride from the following data :—

$$\begin{aligned} 2Al + 6HClaq &= Al_2Cl_6aq + 3H_2 + 240{,}000 \\ H_2 + Cl_2 &= 2HCl + 44{,}000 \\ HCl + aq &= HClaq + 17{,}500 \\ Al_2Cl_6 + aq &= Al_2Cl_6aq + 153{,}700. \end{aligned}$$

(5) The heat of precipitation of AgCl is the same no matter whether it is prepared by any of the following methods :—

(*a*) addition of silver nitrate to hydrochloric acid;

(*b*) addition of potassium chloride to dilute silver nitrate;

(*c*) addition of silver sulphate to sodium chloride solution;

(*d*) addition of barium chloride solution to silver chlorate solution. Explain this.

(6) Describe how you would determine the heat of neutralisation of an acid by a base. Of what importance is this determination?

(7) In what way is the heat of reaction connected with the variation of the equilibrium constant of the reaction with temperature. Give examples of the use of this relationship to determine heats of combustion or formation. (See Chapter VIII, p. 349.)

(8) What is Hess's Law? The heat of solution of anhydrous strontium chloride is 11,000 gm.-cals., and that of the hexahydrate − 7,300 gm.-cals. Calculate the heat of hydration of the anhydrous salt to hexa-hydrate.

(9) Calculate the heats of formation of ethane, ethylene, and acetylene respectively from their elements at 17° C: (*a*) at constant pressure, (*b*) at constant volume, given the following heats of combustion: ethane 370,350 gm.-cals.; ethylene 333,350 gm.-cals.; acetylene 310,000 gm.-cals.

Heats of formation: carbon dioxide, 94,380 gm.-cals.; liquid water, 68,380 gm.-cals.; all taken at constant pressure.

CHAPTER XVI

ENERGY AND CHEMICAL REACTIONS

312. Heat and Energy.—The First Law of Thermodynamics.—Heat is a form of energy. When a body is heated its energy is increased. The Law of Conservation of Energy, which has come to be accepted as universally true by experience, states that energy can neither be created nor destroyed, and, hence, if heat is absorbed by a body, it must be converted into some other form of energy. No fraction of it can be lost.

The First Law of Thermodynamics is the logical outcome of the Law of Conservation of Energy. It states that *mechanical energy and heat energy are quantitatively interconvertible.* The experimental work necessary to prove the validity of this Law was carried out by Joule between 1843 and 1880. He measured the amount of heat produced in a large number of different mechanical processes, and showed that it was related to the energy expended by the relationship

$$E = JQ,$$

where E is the amount of work done, Q the heat developed and J a constant, known as Joule's Equivalent.

This Law is of great importance when a chemical system is being studied, and has already been used in the derivation of Hess's Law of Thermoneutrality (§ 304).

313. Kirchoff's Equation.—This is simply derived from the Law of Conservation of Energy, and concerns the relationship between the specific heats of the reactants and products of a chemical reaction, and the variation of the heat tonality with temperature.

(1) Let the reaction be carried out with 1 gm. of reactants at temperature T and at constant volume. Suppose the amount of heat given out is $-U$.[1]

(2) Heat the products, of which the specific heat is Σc_2 (Σc_2 is the specific heat of all the products dealt with as one body), through a very small temperature, dT. The amount of heat taken in is $\Sigma c_2 dT$.

(3) Let the reaction now be reversed. The amount of heat taken in will be $+(U - dU)$.

[1] Note the convention of signs on p. 629

(4) *Cool the reactants to temperature* T; if Σc_1 is the specific heat of the reactants, the amount of heat given out is $-\Sigma c_1 dT$. The system is now in its original condition. Hence, by the Law of Conservation of Energy,

$$-U + \Sigma c_2 dT + (U - dU) - \Sigma c_1 dT = 0$$

$$\therefore \frac{dU}{dT} = \Sigma c_1 - \Sigma c_2.$$

This is known as Kirchoff's Equation.

314. Reversible and Irreversible Processes.—A reversible change in the thermodynamic sense, is one which can be made to take place in either direction at will, by an infinitesimal alteration in one of the conditions governing the equilibrium (*e.g.*, pressure, temperature, etc.). An irreversible change is one in which an infinitesimal alteration in the conditions causes a spontaneous and complete change in the equilibrium. These changes may be compared with systems in stable and in unstable equilibrium respectively. A reversible change corresponds to the process of moving a body from its position of stable equilibrium; an irreversible change corresponds to the movement of a body from its position of unstable equilibrium. An infinitesimal constraint is, in this case, sufficient to remove the system completely from its state of equilibrium, to which it does not return on removal of the constraint.

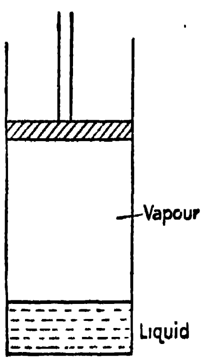


FIG. 190.

Many processes which take place spontaneously can readily be called to mind. Thus, when a gas is admitted to an evacuated vessel, it completely fills the space spontaneously. If a dilute solution is poured carefully on to the top of a more concentrated one, diffusion occurs spontaneously until the two solutions have the same concentration. Some chemical reactions fall into this category. Thus ammonia gas and hydrogen chloride react spontaneously to form ammonium chloride.

These spontaneous reactions always proceed in the direction of greater stability, and free energy decrease.[1] They are also irreversible in the thermodynamic sense. All spontaneous reactions are irreversible.

Many processes are, however, reversible, in the theoretical sense

[1] The free energy of a system is the maximum external work that can be performed by it.

at least. To take an example, we can consider a liquid contained in a frictionless vessel and shut in by a piston. The space above the liquid is filled only with the saturated vapour of the liquid. We will suppose that pressures of varying magnitude can be put on to the piston. If the pressure placed upon it is equal to the vapour pressure of the liquid at the temperature in question, then the system will be in equilibrium, and liquid will neither evaporate nor be formed. If, now, the pressure on the piston is increased by an infinitesimal amount, all of the vapour condenses to liquid. If the pressure on the piston is decreased by an infinitesimally small amount, the liquid will evaporate. Thus, a slight change in pressure on either side of the equilibrium pressure, which is in this case the vapour pressure, results in an alteration in the system. A system of this kind is said to be a reversible system.

We may take as another example the action of heat on calcium carbonate in a vessel closed with a piston.

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The carbon dioxide will exert a certain pressure, called the dissociation pressure, dependent upon the temperature. This may be called p. If the pressure on the pistón be carefully maintained at p, the system is in equilibrium, and will remain so. No calcium carbonate will be decomposed, and none will be formed; at least, this is the apparent state of affairs. Actually, of course, the carbonate is being formed and decomposed at the same rate. If, now, the pressure on the piston be increased to $p + dp$, some carbon dioxide will disappear from the system, and more calcium carbonate will be produced. On the other hand, if the pressure is decreased to $p - dp$, then more calcium carbonate will decompose and more carbon dioxide will be produced in order, once more, to attain equilibrium. This is a typical reversible process.

Another example will be considered briefly, because we shall have occasion to mention it later. It is the reaction which takes place in the Daniell cell, and which can be represented by the equation

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$$

The cell consists of a zinc rod in zinc sulphate solution (or dilute sulphuric acid) and a copper plate in copper sulphate solution, the two solutions being separated by a porous pot. The electromotive force of the cell is 1·09 volts. If, now, an e.m.f. slightly greater than 1·09 volts is applied to the cell, the reaction is reversed, and zinc is formed, whilst copper dissolves. On the other hand, if an e.m.f. a little less than 1·09 volts is applied to the cell, the reaction takes place in the direction represented by the arrow. This electrical process is frequently taken as an example of a reversible process.

It may be mentioned that in practice it is not possible to get a strictly reversible process. Energy is always dissipated in some form, particularly as a result of friction. Any reversible process is necessarily infinitely slow as infinitesimally small forces are applied.

315. The Second Law of Thermodynamics.—There are several ways of expressing the Second Law of Thermodynamics, but the best for our purposes are :—

"*It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at a low to one at a higher temperature,*" or

"*Heat cannot of itself* (*i.e.*, without the performance of work by some external agency) *pass from a colder to a warmer body.*"

This Law has important bearings in practice, both in chemistry and in physics, but in order to see what limitations it places on physical processes, let us consider the conversion of electrical energy into mechanical work. These two are interconvertible, and an electric motor could be constructed to give an efficiency of 100 per cent., theoretically. Of course, it rarely exceeds 90 per cent., owing to losses due to friction, etc. Similarly, a dynamo, working in the reverse way to a motor, could be constructed of very high efficiency. But when we consider a heat engine, such as a steam engine, we find that its conversion of heat into work is strictly limited by the Second Law of Thermodynamics, for heat cannot of itself pass from a colder to a warmer body.

316. Efficiency of a Reversible Process.—This can be calculated by finding the work done when a perfect gas is taken through a cycle of reversible operations, and comparing it with the amount of heat taken in during the change. The treatment of this problem is due to Carnot, and the system taken is generally known as Carnot's cycle.

I. The first stage is to take one gram-molecule of a perfect gas in a cylinder provided with a frictionless piston. The volume of the gas is v_1 c.c. The cylinder is placed in contact with a "source," a heat reservoir of such a size that the abstraction of a small quantity of heat does not affect its temperature. The temperature of the source is T_2. The gas is allowed to expand isothermally to a volume v_2. The amount of work done by the gas A is given by (§230),

$$A = RT_2 \log_e \frac{v_2}{v_1}$$

and is represented by the area ABQP (Fig. 191). An amount of heat Q will have been taken from the source.

II. The cylinder is removed from the source and completely

thermally insulated. The gas is allowed to expand adiabatically (§ 195) until the temperature has fallen to T_1. The volume of the gas is v_3. v_3 is connected with v_2 by the expression (§78)

$$\frac{T_2}{T_1} = \left(\frac{v_3}{v_2}\right)^{\gamma} \qquad (1)$$

where γ is the ratio of the specific heats.

During this process, an amount of external work is done, equal to the area BCRQ. No heat is, however, taken up or given out.

III. The cylinder is now placed in contact with a "sink"—a heat reservoir which will take up heat. The temperature of the sink

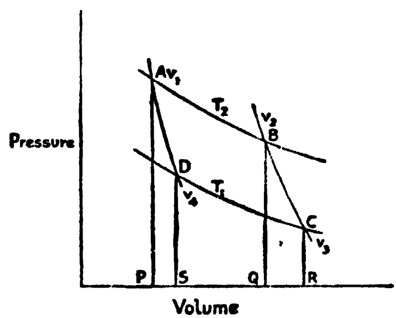


FIG. 191.—Carnot's Cycle.

is T_1. The gas is compressed isothermally until the volume is v_4. The amount of work done on the gas A_1 is equal to $RT_1 \log_e \frac{v_3}{v_4}$. An amount of heat Q_1, equivalent to the work A_1, is given up to the sink. The amount of work done A_1 is equal to the area CDSR.

IV. The cylinder is again insulated, and the gas compressed adiabatically until its volume is v_1, and temperature T_2. The amount of work done on the gas is equal to the area ADSP, but no heat transference is involved in the change. T_1 and T_2 are now connected by the equation

$$\frac{T_1}{T_2} = \left(\frac{v_1}{v_4}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

During the total change, the amount of work done is equal to the area of the figure ABCD. From (1) and (2) it follows that

$$\frac{v_3}{v_2} = \frac{v_4}{v_1},$$

and that the two adiabatic changes are therefore identical as regards the numerical quantity of work done. In one case, however,

it is done on the gas, and in the other by the gas, so that the net amount of work involved in the adiabatic changes is zero.

The external work gained in the change is $A_2 - A_1$. This has been done at the expense of an amount of heat $Q_2 - Q_1$. The efficiency of the process is given by

$$\frac{\text{Heat transformed into work}}{\text{Heat drawn from supply}} = \frac{Q_2 - Q_1}{Q_2} = \frac{A_2 - A_1}{A_2}.$$

But, $$A_2 = RT_2 \log_e \frac{v_2}{v_1}, \text{ and } A_1 = RT_1 \log_e \frac{v_3}{v_4}.$$

$$\therefore \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now let A stand for the external work done by the gas, and Q the heat absorbed. Then

$$A = Q \, . \, \frac{T_2 - T_1}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It follows that the maximum efficiency of a heat engine is dependent only upon the temperatures between which it works, and not at all on the working substance. The heat engine corresponding to this theoretical cycle cannot, of course, be constructed practically. As has been mentioned in §314, a reversible process such as this would be infinitely slow.

317. Work and Chemical Reactions.—It is a general rule that "*The maximum external work which can be done by a physical or chemical change is only obtained when the change takes place reversibly.*"

We have already referred to the meaning of reversibility in the thermodynamic sense. It is now necessary for us to understand that the maximum external work can only be obtained when a chemical reaction takes place under thermodynamically reversible conditions.

If we consider a reservoir of compressed air, it would be easy to waste all the energy latent in it by allowing it to blow off into a vacuum. No work would then be done by the gas. In order to do the most work with the gas, it is obvious that it will have to be made to push out a piston, and only the minimum excess of pressure required to do this should be used. If more than this is applied, it will be wasted. This, however, is just the condition for reversibility, and so we conclude that the most efficient process is a reversible one.

Consider a chemical reaction which takes place with absorption or evolution of heat. The reactants possess a certain amount of internal energy, part of which is released when the reaction takes place. This decrease in the internal energy of the system is denoted by U. In the general case, the energy released may be given out

as heat, and a certain amount of external work may be done. Let Q be the amount of heat absorbed by the reaction ($-Q$ is the amount evolved), and let A be the amount of external work done by the reaction. Then, by the First Law,

$$U = A - Q.$$

U, Q and A may be positive, negative or zero, but always the above equation is true.

In dealing with quantities of heat, the sign is important. Heat *flowing in* to a system is *positive*; heat *flowing out* is *negative*. The truth of the above equation is shown by considering the case where no external work is done, *viz.*, when the reaction is carried out in a calorimeter. Here $A = 0$, and it follows from the equation that $U = -Q$, *i.e.*, the decrease in the internal energy of the system is equal to the amount of heat *evolved* by the reaction.

A is frequently called the change of *free energy* associated with the process.

318. The Gibbs-Helmholtz Equation, and its Application to the Daniell Cell.—Using the terms as defined in the last section, the First Law of Thermodynamics leads to the equation

$$U = A - Q \quad \ldots \ldots \ldots \quad (1)$$

With this notation, a positive value of U means a decrease of internal energy in the reaction. This equation is perfectly general and applies not only to chemical reactions, but to any system in which internal energy is converted into heat and external work.

As proved in § 316, the efficiency of a reversible process is given by

$$\frac{A}{Q} = \frac{T_2 - T_1}{T_2},$$

or

$$\frac{dA}{Q} = \frac{dT}{T}.$$

$$\therefore \quad Q = T\frac{dA}{dT}.$$

Substituting this value in (1), we have

$$U = A - T\frac{dA}{dT},$$

which is known as the *Gibbs-Helmholtz equation*.

From this equation, a number of important deductions may be made.

(*a*) In order that A should equal U, $T\frac{dA}{dT}$ must be equal to zero. This may happen in two ways, either T can be 0, or dA/dT may be 0.

Thus, if $dA/dT = 0$, the free energy, A, of the process is independent of temperature. Taking the Daniell cell for example, the temperature coefficient of the e.m.f. is almost zero, and hence in the reaction

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4,$$

A is almost equal to U. This will be mentioned again later. At absolute zero, too, $A = U$.

(*b*) Since $U = A - Q$, $Q = A - U$. Substituting in the Gibbs-Helmholtz equation, we have

$$Q = A - U = T\frac{dA}{dT}.$$

Hence, the sign of the heat change in a chemical reaction depends upon the sign of $T\frac{dA}{dT}$, *i.e.*, of $\frac{dA}{dT}$. Thus, a reaction will be endothermic (*i.e.*, heat will be taken in) if $\frac{dA}{dT}$ is positive; it will be exothermic (*i.e.*, heat will be given out) if $\frac{dA}{dT}$ is negative.

319. The Clapeyron-Clausius Equation, and its Application to Elevation of Boiling Point and Depression of Freezing Point.—The Clapeyron-Clausius equation is a straightforward application of the Gibbs-Helmholtz equation to a simple system.

The example of a liquid and its vapour confined in a cylinder by a frictionless piston has already been considered as an illustration of what is meant by a reversible system. Suppose that we have 1 gm. of liquid confined in a cylinder under a piston with pressure p equal to the vapour pressure of the liquid (Fig. 190). Now allow the liquid to evaporate at a constant temperature T. The piston will move out because the vapour now occupies a greater volume. If the vapour of the liquid occupies a volume v' and the original volume of the liquid was v, the amount of external work done, A, is given by

$$A = p(v - v').$$

In evaporating, however, an amount of heat equal to the latent heat was absorbed, and since, the evaporation was supposed to take place at constant temperature, this energy must come from surrounding bodies, which are cooled. Thus, the heat absorbed is l, the latent heat.

Hence, $$U = p(v - v') - l.$$

Substituting these values in the Gibbs-Helmholtz equation, we have

$$A - U = T\frac{dA}{dT}.$$

$$l = T\frac{dp}{dT}(v - v'),$$

which is the *Clapeyron-Clausius equation.*

If the volume of liquid is neglected compared with that of the vapour,

$$l = T\frac{dp}{dT}v,$$

which can now be readily integrated, if it is supposed that l does not vary with temperature. This is only true over small temperature ranges.

The gas law states $$v = \frac{RT}{Mp}$$

$$\therefore\ l = \frac{RT^2}{Mp}\cdot\frac{dp}{dT},$$

where M is the molecular weight. If $Ml = L$, the molecular latent heat, we have

$$L = \frac{RT^2}{p}\cdot\frac{dp}{dT}, \text{ or } \frac{dT}{T^2} = \frac{R}{L}\cdot\frac{dp}{p},$$

$$\log_e\frac{p_2}{p_1} = \frac{L}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where p_1 and p_2 are the vapour pressures at T_1 and T_2.

Throughout the above, it has been assumed that the vapour acts as a perfect gas.

Elevation of Boiling Point.—The Clapeyron-Clausius equation may be used to obtain the molecular elevation from the latent heat. If there is an elevation δT when w gms. of a solute are dissolved in 100 gms. of solvent, and M is the molecular weight of the solute, the molecular elevation, k, is given by the equation

$$k = \frac{M\delta T}{w},$$

If the boiling point of the pure solvent is T, and that of the solution $T + \delta T$ when the atmospheric pressure is p_1, then

p_1 is the vapour pressure of the solution at $T + \delta T$ and is also the vapour pressure of the solvent at T, and

p_2 is the vapour pressure of the solvent at $T + \delta T$.

p_2 may be calculated from the Clapeyron-Clausius equation, since

$$\log_e\frac{p_2}{p_1} = \frac{L}{R}\left\{\frac{1}{T} - \frac{1}{T + \delta T}\right\},$$

$$= \frac{L}{R}\,\frac{\delta T}{T(T + \delta T)},$$

$$= \frac{L\delta T}{RT^2}, \text{ when } \delta T \text{ is very small.}$$

Now $\log_e \frac{p_2}{p_1} = \log_e \left(1 + \frac{p_2 - p_1}{p_1}\right) = \frac{p_2 - p_1}{p_1}$, the remainder of the terms being neglected, since $p_2 - p_1$ will be small.

By Raoult's Law, $\frac{p_2 - p_1}{p_2} = \frac{n}{N}$, where n = number of molecules of solute and N = that of solvent. When the difference between p_2 and p_1 is very small, as has just been supposed, $\frac{p_2 - p_1}{p_2}$ may be taken to be equal to $\frac{p_2 - p_1}{p_1}$;

$$\therefore \frac{n}{N} = \frac{L\delta T}{RT^2}.$$

But $n = \frac{w}{M}$, where M = molecular weight of solute, and $N = \frac{100}{M'}$, where M' = molecular weight of solvent.

$$\therefore \frac{wM'}{100M} = \frac{L\delta T}{RT^2},$$

$$\delta T = \frac{RT^2wM'}{100ML}.$$

Hence, $$k = \frac{M\delta T}{w} = \frac{M}{w} \cdot \frac{RT^2wM'}{100ML} = \frac{M'}{L} \cdot \frac{RT^2}{100}$$

But $$L/M' = l,$$

$$\therefore k = \frac{RT^2}{100l}.$$

Putting R = 2 gm.-cals., we have

$$k = \frac{0{\cdot}02T^2}{l}.$$

Depression of the Freezing Point.—A similar calculation gives the expression

$$k' = \frac{0{\cdot}02T^2}{l}$$

for the molecular depression of the freezing point, where l is now the latent heat of fusion.

320. Chemical Affinity.—It is only with the advent of clearer views on the energy relationships of chemical reactions that the subject of chemical affinity has been studied with fruitful results.

In the early history of chemistry, affinity was judged by the power that a substance had of turning another out of combination. Thus, if the reaction indicated by the upper arrow in the equation

$$AB + C \rightleftharpoons A + BC$$

took place, then it was supposed that B had a smaller affinity for A than C had, for C was able to turn B out of its combination with A.

By studying reactions, particularly the neutralisation of acids by bases, a "table of affinity" was drawn up showing the relative affinities of a series of bases for a given acid, or *vice versâ*.

However, in these early attempts the question of volatility of one of the products or reactants was never taken into account, and it later became recognised that reactions were sometimes reversible under ordinary conditions, and that if the conditions were properly chosen it was possible to cause almost every reaction to take place in the reverse direction. If a certain substance had a fixed and unalterable affinity towards an acid, say, how would it be possible for it to turn it out of combination, whilst at the same time the reverse reaction is taking place? Berthollet, as we have seen, solved the problem by stating that the direction in which a chemical reaction takes place is dependent upon the active masses of the reactants, as well as upon their affinities. Thus, the direction of the reaction gave no certain indication of the affinity of one substance for another, since deficiencies in affinity could be made up for by increase in concentration.

Later, it was recognised that the energy of a reaction had a great deal to do with affinity. As a rule, a reaction in which a good deal of heat is given out goes on rapidly, whilst one in which little heat is given out is usually slow; so it was thought that the heat of reaction could be used as an index of the affinity.

This was soon shown to be incorrect, however, since, if it were correct, reactions could only proceed in the direction in which heat was given out. Exothermic reactions would be the only possible ones. Yet endothermic reactions could take place just as readily as exothermic ones. Obviously, this was a very serious argument against the theory.

It has been shown, however, that the chemical affinity of a reaction is not the total decrease of internal energy of the system, U, but is the maximum external work, A, that the reaction can do when carried out reversibly (in the thermodynamic sense), and isothermally. This is also called the "free energy" of the reaction. The objection raised by the existence of endothermic reactions can be over-ridden by a consideration of the Gibbs-Helmholtz equation. It has already been shown that an endothermic reaction is one for which $\frac{dA}{dT}$ is positive. The sign of A is not directly concerned with this. The affinity of a reaction may increase or decrease with temperature (*i.e.*, $\frac{dA}{dT}$ may be negative or positive) without the affinity being negative.

The measurement of affinity, therefore, depends on the measurement of the "free energy" of the reaction, and this can be done in several ways. The maximum work will be available when the reaction is carried out reversibly (in the thermodynamic sense).

In the first method, the Gibbs-Helmholtz equation is made use of. A method of making the reaction go on reversibly is to carry it out in an electrical cell, allowing the cell to supply energy at an infinitely slow rate. Thus, considering the reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$$

The affinity of this can be found by making up a Daniell cell, and measuring its e.m.f. by means of a potentiometer, when no current is taken from the cell. The available energy of the cell per gram-equivalent of zinc dissolved is FE, where F is the quantity of electricity which passes round the circuit during the solution of the zinc, and E is the e.m.f. F has the value 96,500 coulombs, and is the same for one equivalent of any element. Hence, the affinity of the reaction which goes on in the Daniell cell is

$$\begin{aligned} A = 1{\cdot}09 \times 96{,}500 &= 105{,}195 \text{ joules per equiv.} \\ &= \frac{105{,}195}{4{\cdot}189} \text{ gm.-cals. per equiv.} \\ &= 25{,}112 \text{ gm.-cals. per equiv.} \\ &= 50{,}224 \text{ gm.-cals. per gm.-mol.} \end{aligned}$$

The Gibbs-Helmholtz equation enables us to arrive at this in another way. If we know the value of the total internal energy, which can be found by carrying out the reaction in a calorimeter without performance of external work, and the rate of change of affinity with temperature, which is obtained from the temperature coefficient of the e.m.f. of the cell, we can substitute in the equation and find A. For the Daniell cell, $U = 50{,}110$ gm.-cals. per gm.-mol. and $TdA/dT = 430$.

Since
$$\begin{aligned} A &= U + T\frac{dA}{dT} \\ A &= 50{,}110 + 430 \\ &= 50{,}540 \text{ gm.-cals. per gm.-mol.} \end{aligned}$$

The agreement between the values obtained by the two methods is seen to be very close.

Of course, it is not always possible to carry out any desired reaction in an electrical cell, and so this method is not always applicable.

Where there is a change in vapour pressure, or in solubility (*i.e.*, alteration of osmotic pressure) the free energy change can be readily calculated. Thus, suppose we consider the affinity of anhydrous copper sulphate for water. If p_0 is the vapour pressure of water

at the temperature considered, and p_1 is that over the crystals, then the amount of work done in expanding isothermally and reversibly 1 gm.-molecule of water vapour from p_0 to p_1 is a measure of the affinity of the reaction $CuSO_4 + 5H_2O = CuSO_4.5H_2O$ The amount of work thus done is

$$A = \int_{p_0}^{p_1} pdV = -\int_{p_0}^{p_1} Vdp = -RT\log_e\frac{p_1}{p_0} = RT\log_e\frac{p_0}{p_1},$$

the water vapour being supposed to behave as a perfect gas. The value is given in gram-calories per gram-molecule of water. As an example of this, the affinity of sodium sulphate for water in the formation of the decahydrate at 15° C. may be calculated. At this temperature, the dissociation pressure of the hydrate is 9·7 mm. and the vapour pressure of water 12·7 mm.

Here $p_0 = 12{\cdot}7$ mm.
$p_1 = 9{\cdot}7$ mm.

$$A = -\int_{p_0}^{p_1} Vdp = RT\log_e\frac{p_0}{p_1}$$

$$= 2 \times 288 \log_e \frac{12{\cdot}7}{9{\cdot}7} \text{ per gram-molecule of water vapour.}$$

$$= 2 \times 288 \times 2{\cdot}303 \log_{10}\frac{12{\cdot}7}{9{\cdot}7}$$

$$= 155{\cdot}2 \text{ gram-calories per gram-molecule of water.}$$

The affinity can also be determined from a knowledge of equilibrium constants. The theory of the method is best derived by considering van't Hoff's "equilibrium box." When equilibrium is attained in any system, it is clear that the free energy has reached a minimum.

The "equilibrium box" is a theoretical device by means of which the reaction

$$A + B \rightleftharpoons C + D$$

can be made to take place by a series of reversible operations. It is supposed to have one wall permeable to A, another to B, another to C and another to D.

It is supposed, for the sake of simplicity, that the reactants and products are perfect gases. Let p_a and p_b be the initial pressures of A and B. The equilibrium pressures are P_A, P_B, P_C and P_D. The final pressures of C and D are p_c and p_d.

(1) Alter the pressure on A from the initial to the equilibrium

pressure. The work done by the gas is

$$\int_{P_A}^{p_a} v.dp = RT \log_e \frac{p_a}{P_A}.$$

(2) Do the same with B, the work done by the gas being

$$\int_{P_B}^{p_b} vdp = RT \log_e \frac{p_b}{P_B}.$$

(3) Introduce the gases into the "equilibrium box" through their respective semi-permeable walls. No work is done in this process. Here they react producing C and D at the equilibrium pressures. Again this involves no work, since the reactants and the products are at their equilibrium concentrations.

(4) C and D are now removed through their respective walls, no work being required for this operation.

(5) They are reduced to the final pressures. The work done by the gases in this process is, by C,

$$\int_{p}^{P_C} vdp = RT \log_e \frac{P_C}{p_c},$$

$$\text{and by D, } RT \log_e \frac{P_D}{p_d}.$$

The total work which has been performed by the gases is

$$A = RT \log_e \frac{p_a}{P_A} + RT \log_e \frac{p_b}{P_B} + RT \log_e \frac{P_C}{p_c} + RT \log_e \frac{P_D}{p_d}.$$

$$A = RT \log_e \frac{P_D P_C}{P_A P_B} - RT \log_e \frac{p_d p_c}{p_a p_b}.$$

Since, for perfect gases, pressures are proportional to concentrations,

$$A = RT \log_e K - RT \log_e \frac{p_d p_c}{p_a p_b},$$

where K is the equilibrium constant.

In the generalised form, for the reaction

$$n_1 A_1 + n_2 A_2 + \ldots \rightleftharpoons n_1' A_1' + n_2' A_2' + \ldots$$

$$A = RT \log_e K - RT \log_e \frac{[A_1']^{n_1'} [A_2']^{n_2'} \ldots}{[A_1]^{n_1} [A_2]^{n_2} \ldots}$$

or

$$A = RT \log_e K - RT \Sigma n \log_e C.$$

This is generally known as the *van't Hoff isotherm*. If we start

with 1 gm.-molecule of each reactant, and finish with one of each product, and the pressure is taken as one atmosphere, then the final term disappears, and the isotherm becomes

$$A = RT \log_e K.$$

As an example of the use of the van't Hoff isotherm, the affinity of hydrogen for iodine when they combine to give hydrogen iodide may be calculated.

$$H_2 + I_2 \rightleftharpoons 2HI.$$

According to Bodenstein, at 443° C., $K = 50{\cdot}62$.

Hence,

$$A = RT \log_e K = 2 \times 716 \times 2{\cdot}303 \times \log_{10} 50{\cdot}62 = 5{,}619 \text{ gm.-cals.}$$

Since there is no change in pressure as a result of the reaction, the second term of the isotherm disappears.

At 500° C., $K = 41$, hence

$$A = RT \log_e K = 2 \times 773 \times 2{\cdot}303 \log_{10} 41 = 5{,}760 \text{ gm.-cals.}$$

The *Nernst Heat Theorem* may be made use of in calculating affinity, and does, in fact, give us the variation of affinity with temperature.

It is not possible to use the Gibbs-Helmholtz equation in the reverse direction, *i.e.*, it is not possible to calculate the affinity of a reaction if we know the calorific value, since the equation cannot be integrated without bringing in a constant of integration, the value of which is not known directly. It is the purpose of the Nernst Heat Theorem to evaluate the constant of integration, I, which is called the "chemical constant."

The Gibbs-Helmholtz equation is

$$A - U = T\frac{dA}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which can be rewritten

$$T\frac{dA}{dT} - A = -U.$$

Dividing through by T^2

$$\frac{I}{T}\frac{dA}{dT} - \frac{A}{T^2} = -\frac{U}{T^2}$$

i.e.,

$$\frac{d}{dT}\left(\frac{A}{T}\right) = -\frac{U}{T^2}.$$

Integrating, we have

$$\frac{A}{T} = -\int \frac{U}{T^2}\,.\,dT + I \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To find the value of I we must consider what happens to A and U

at the absolute zero. The curve below shows the effect of temperature on them. According to Nernst, both A and U become identical at the absolute zero, and, indeed, at a few degrees before this. Both curves also become parallel to the temperature axis. This gives the clue to the solution of the problem, for it means that both dA/dT and dU/dT are zero when T is zero. This is the Nernst Heat Theorem.

The effect of temperature on U may be expressed by a series of terms in ascending powers of T.

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots \quad . \quad . \quad . \quad (3)$$

Equation (2) becomes

$$\frac{A}{T} = I - \int\left(\frac{U_0}{T^2} + \frac{\alpha}{T} + \beta + \gamma T + \ldots\right) dT.$$

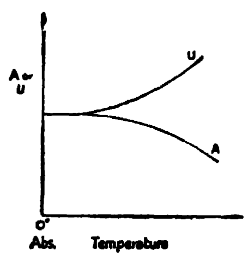


FIG. 192.—Graph of A and U against Temperature, T.

Integrating,

$$\frac{A}{T} = I - \left(-\frac{U_0}{T} + \alpha \log_e T + \beta T + \frac{\gamma T^2}{2} + \ldots\right)$$

$$\therefore \quad A = IT + U_0 - \alpha T \log_e T - \beta T^2 - \frac{\gamma T^3}{2} - \ldots \quad . \quad (4)$$

But $$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots$$

According to Nernst,

$$\frac{dA}{dT} = 0, \text{ and } \frac{dU}{dT} = 0, \text{ when } T = 0.$$

From equation (4),

$$\frac{dA}{dT} = I - \alpha - \alpha \log T - 2\beta T - \frac{3}{2}\gamma T^2 - \ldots \quad . \quad (5)$$

From equation (3),

$$\frac{dU}{dT} = \alpha + 2\beta T + 3\gamma T^2 + \ldots \quad . \quad . \quad . \quad . \quad (6)$$

Putting $T = 0$ in equation (5),

$$\frac{dA}{dT} = I - \alpha - \alpha \log 0.$$

According to the Nernst Heat Theorem, $\frac{dA}{dT}$ must be zero under these conditions. This can only happen if both I and α are zero, since $\alpha \log 0$ would otherwise be infinite. When α also is zero, the indeterminate $\alpha \log 0$ may be zero. Hence, from equation (5),

$$\frac{dA}{dT} = -2\beta T - \frac{3}{2}\gamma T^2 - \ldots$$

or, from (4),

$$A = U_0 - \beta T^2 - \frac{\gamma}{2}T^3 - \ldots \quad . \quad . \quad . \quad . \quad (7)$$

Applying the other part of the Nernst Heat Theorem, *viz.*,

$$\frac{dU}{dT} = 0,$$

when $T = 0$, we obtain again $\alpha = 0$.

$$U = U_0 + \beta T^2 + \gamma T^3 + \ldots \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Another relationship is derived from Kirchoff's equation (§ 313), *viz.*,

$$c_1 - c_2 = \frac{dU}{dT},$$

where c_1 is the specific heat of the reactants, and c_2 that of the products.

Hence,

$$c_1 - c_2 = 2\beta T + 3\gamma T^2 + \ldots \quad . \quad . \quad . \quad . \quad (9)$$

Neglecting γ we can obtain β from (9). Substituting this in (8), and measuring U, we can find a value for U_0. Now, substituting for β and U_0 in (7), we have A in terms of T.

The Nernst Heat Theorem has been applied to many cases of chemical equilibrium. As an example, we may take the calculation of the transition point of sulphur. From observations of the difference between the specific heats, $2\beta = 1{\cdot}15 \times 10^{-5}$

Now

$$A = U - 2\beta T^2.$$

U is known to be 1·57 from determinations of the heat of transformation. Hence, $A = 1{\cdot}57 - 1{\cdot}15 \times 10^{-5}T^2$.

$A = 0$, when

$$\sqrt{\frac{1{\cdot}57}{1{\cdot}15 \times 10^{-5}}} = 369{\cdot}5° \text{ Abs.}$$

This will be the transition point, since at this point the free energy will be zero. The value obtained is thus 96·5° C. The observed value is 95·6° C.

The equation can also be used to calculate the melting points of

substances, since these are merely the transition points of the solid form being converted into the liquid form. It has also been used for the calculation of the e.m.f. of cells.

321. The van't Hoff Isochore.—We have already derived the relationship known as the van't Hoff isotherm, *viz.*,

$$A = RT \log_e K - RT \log_e \frac{p_d p_e}{p_a p_b},$$

or, in the general case,

$$A = RT \log_e K - RT\Sigma n \log_e C.$$

It is now required to find how the equilibrium constant, K, varies with temperature. This can readily be done by differentiating the isotherm with respect to temperature. If the volume is kept constant, we have

$$\left(\frac{dA}{dT}\right)_v = R \log_e K + RT\frac{d}{dT}(\log_e K)$$
$$- R\Sigma n \log_e C - RT\frac{d}{dT}(\Sigma n \log_e \mathrm{C}).$$

Since n and $\log_e C$ are not in any way connected with the temperature,

$$RT\frac{d}{dT}(\Sigma n \log_e \mathrm{C}) = 0.$$

$$\left(\frac{dA}{dT}\right)_v = R \log_e K + RT\frac{d}{dT}(\log_e K) - R\Sigma n \log_e C.$$

$$T\left(\frac{dA}{dT}\right)_v = RT \log_e K + RT^2\frac{d}{dT}(\log_e K) - RT\Sigma n \log_e C.$$

But $$A = RT \log_e K - RT\Sigma n \log_e C$$

$$\therefore \quad T\left(\frac{dA}{dT}\right)_v = A + RT^2\frac{d}{dT}(\log_e K).$$

The Gibbs-Helmholtz equation (§ 318) states that

$$A - U = T\left(\frac{dA}{dT}\right)_v,$$

$$\therefore \quad RT^2\frac{d}{dT}\log_e K = -U,$$

or $$\frac{d}{dT}\log_e K = -\frac{U}{RT^2}.$$

For U we can write $-Q_v$, where Q_v is the heat absorbed by the reaction when carried out at constant volume. This is true, since no external work is done when the reaction is carried out at constant volume. The equation now becomes

$$\frac{d}{dT}\log_e K = \frac{Q_v}{RT^2}.$$

This is known as the *van't Hoff isochore*, and is the quantitative form of the Le Chatelier-Braun principle of mobile equilibrium (§ 138). Like the latter, it can be applied to all kinds of systems, not only to chemical reactions.

In applying the van't Hoff isochore to any particular case, it is necessary to integrate the expression, which cannot be used as it stands. The problem, then, is to integrate the equation

$$\frac{d}{dT}\log_e K = \frac{Q_v}{RT^2}.$$

It is necessary first of all to make an assumption concerning Q_v, *i.e.*, that it is independent of temperature over a small range. Practically, this is not quite true, but sufficiently nearly so to enable the calculation to be made, and the result applied with fair accuracy.

We have then

$$\int_{K_1}^{K_2} d(\log_e K) = \int_{T_1}^{T_2}\frac{Q_v\,.\,dT}{RT^2},$$

$$\log_e\frac{K_2}{K_1} = \frac{-Q_v}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \frac{-Q_v}{R}\left(\frac{T_1-T_2}{T_1T_2}\right).$$

As an example of the use of this equation, we may take the dissociation of nitrogen tetroxide,

$$N_2O_4 \rightleftharpoons 2NO_2.$$

The equilibrium constant of this reaction $\left(\frac{[NO_2]^2}{[N_2O_4]}\right)$ is 0·0017 at 27° C. and 1 atmosphere. At 111° C. the equilibrium constant is 0·204. It is required to calculate the heat of dissociation per gram-molecule.

We first of all convert the isochore into logarithms to the base 10, and then substitute the values given.

$$\log_{10}\frac{K_2}{K_1} = \frac{-Q_v}{2\cdot303\,R}\left(\frac{T_1-T_2}{T_1T_2}\right)$$

$$K_2 = 0\cdot0017,\quad T_2 = 27 + 273 = 300^\circ \text{ Abs.}$$
$$K_1 = 0\cdot204,\quad T_1 = 111 + 273 = 384^\circ \text{ Abs.}$$
$$R = 1\cdot987 \text{ gm.-cals. per degree}$$

$$\therefore\ \log_{10}\frac{0\cdot0017}{0\cdot204} = \frac{-Q_v}{4\cdot576}\left(\frac{84}{300\times384}\right)$$

$$\therefore\ Q_v = +\ 14{,}400 \text{ gm.-cals.}$$

Hence, the heat absorbed per gram-molecule is 14,400 gm.-cals. A further example is given in Chapter VIII. (§ 159).

Another application of the isochore is the calculation of the ionic

product for water when the temperature coefficient of the conductivity is known. This is done in Chapter XIII., p 558.

The isochore is of very general application. Thus it is possible to calculate the heat of solution of a solid from the temperature coefficient of the solubility, the heat of dissociation of a weak electrolyte from the temperature coefficient of the dissociation constant, etc.

322. Electrochemistry.—The use of the voltaic cell for the calculation of affinity has already been referred to. It is necessary to gain some idea of the relationship of the electromotive force to chemical reactions taking place inside the cell.

The necessity for the use of standard electrodes, and a description of the standard hydrogen electrode, with the derivation of the formula governing the e.m.f. of a concentration cell, have already been given in Chapter XIII., p. 551. We must now go into the subject a little more closely.

Consider a concentration cell of the type

M_1	|	solution containing M_1 ions	|	solution containing M_2 ions	|	M_2
ν_1						E_2

where M_1 and M_2 are two metals. It will possess an e.m.f. given by the formula (§ 277)

$$E_1 - E_2 = \frac{RT}{nF} \log_e \frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the valency of the ions, F is the Faraday, c_1 and c_2 are the concentrations of the ions, and R is the gas constant. In the derivation of this formula the potential at the junction of the liquids was neglected. If now we make one of the electrodes a standard one, it is obviously possible to determine the e.m.f. due to an electrode of any other metal dipping into a solution of one of its salts. Thus, if we make one electrode the normal hydrogen electrode, the potential of which we have arbitrarily set at zero, and use as the other the metal tin dipping into a solution of stannous chloride of known concentration, we shall be able to measure the potential due to the tin.

This potential is, according to Nernst's theory, due to the tendency of the metal to pass into solution in the form of its ions. The electrode potential is the potential developed when a metal is in contact with a normal solution of its ions. In this case c_2 in equation (1) = 1, and if E_0 is the electrode potential

$$E_1 - E_0 = \frac{RT}{nF} \log_e c_1.$$

The Table gives some of the values obtained :—

TABLE CV.

Metal.	Ion.	Potential, volts.	Metal.	Ion.	Potential, volts.
Li	Li^+	− 2·96	Tl	Tl^+	− 0·33
Rb	Rb^+	− 2·92	Co	Co^{++}	− 0·29
K	K^+	− 2·92	Ni	Ni^{++}	− 0·23
Ba	Ba^{++}	− 2·80	Sn	Sn^{++}	− 0·14
Na	Na^+	− 2·71	Pb	Pb^{++}	− 0·12
Mg	Mg^{++}	− 1·55	Fe	Fe^{+++}	− 0·045
Al	Al^{+++}	− 1·28	H	H^+	0·00
Mn	Mn^{++}	− 1·10	Cu	Cu^{++}	+ 0·34
Zn	Zn^{++}	− 0·76	Hg	Hg_2^{++}	+ 0·80
Fe	Fe^{++}	− 0·44	Ag	Ag^+	+ 0·80
Cd	Cd^{++}	− 0·40	Au	Au^{++}	+ 1·36

This is the electronegative series of the metals. A metal having a negative potential has a greater tendency to go into solution as its ions than hydrogen has. It follows that if a metal having a certain potential is placed in a solution containing ions of a metal of a more positive potential, then the former will dissolve, and the ions of the metal in solution will be discharged and the element will be precipitated. Thus, if zinc is placed in a solution of copper sulphate, the zinc has a considerable negative potential, *viz.*, − 0·76 volt, whilst copper has a positive potential of 0·33 volt. Thus, zinc goes into solution, and the copper is precipitated, since the zinc has a greater tendency to dissolve as ions than the copper has. Lead, it is seen, will also precipitate copper from solution.

It is possible to determine the potential of certain non-metallic elements, but there are numerous difficulties. The following values have been obtained :—

TABLE CVI.

Element.	Ion.	Potential., v.
I	I^-	+ 0·54
O	OH^-	+ 0·40
Br	Br^-	+ 0·99
Cl	Cl^-	+ 1·36
F	F^-	+ 1·90

This matter has been dealt with in the simplest possible way. It should be realised that the equation from which the electrode

potentials are calculated is not quite exact, and that the effect of pressure has been neglected. There are numerous refinements which cannot be discussed here.

If the standard electrode potentials of the elements are plotted against their atomic numbers, it is found that the electrode potential is a fundamental property of the element. There is quite a definite periodicity governed by the grouping of the periodic table. It is clear that this should be so, for the tendency of a substance to form ions depends upon the ease in which one electron or more can be lost from the electron shells round the nucleus. This will vary with the number present in the outer shell.

The electrode potential of a metal is *one* of the factors that decides whether it will dissolve in a dilute acid with evolution of hydrogen. The elements with negative potentials dissolve in dilute acids the more readily the greater the numerical value of the potential. It is not to be expected that copper will dissolve in dilute sulphuric acid, since the tendency for copper ions to go into solution is less than that for hydrogen ions to come out of it (the metal has a positive electrode potential). It must however be remembered that the strength of the acid may modify the electrode potential, that the above remarks refer only to normal solutions, and that there are other factors which must be taken into account if the question is to be studied fully.

323. Oxidation and Reduction Potentials.—In ionic processes, oxidation means an increase in the number of positive (or decrease in the number of negative) charges. Reduction is the reverse of this. In a mixed solution of ferrous and ferric ions, the solution will possess oxidising or reducing powers according as whether it can gain or lose electrons. Thus, if a platinum plate is dipped into such a solution, and the mixture tends to oxidise the plate, it will tend to remove electrons from the plate, thus giving it a positive charge; if it tends to reduce the plate, it will seek to give up electrons to the plate, giving it a negative charge. It is clear that the oxidising or reducing power of a solution may be measured by the magnitude and sign of the charge given to the platinum electrode. This charge gives rise to an electrode potential similar to those previously considered. If the platinum electrode in the solution is connected with a normal hydrogen electrode and the e.m.f. of the cell is measured, the value of the electrode potential may be obtained.

The solution will contain Fe^{+++}, Fe^{++} and H^+ ions. The last are, of course, necessary for the reaction to proceed. The reaction occurring is

$$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}.$$

This may be regarded as an oxidation of the Fe^{++} by hydrogen ion,

which is thereby reduced to hydrogen gas. The equation may therefore be written

$$Fe^{+++} + \tfrac{1}{2}H_2 \rightleftharpoons Fe^{++} + H^+.$$

The equilibrium in the system is therefore governed by the equation

$$\frac{[Fe^{+++}]\,(p_{H_2})^{\frac{1}{2}}}{[Fe^{++}]\,[H^+]} = K' \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K' is the equilibrium constant, and p_{H_2} is the pressure of hydrogen gas. The platinum electrode may now be regarded as functioning as an ordinary hydrogen electrode, the potential of the electrode depending upon the hydrogen ion concentration and the pressure of the hydrogen gas. The potential will be given by

$$E = \frac{RT}{F}\log_e\frac{[H^+]}{(p_{H_2})^{\frac{1}{2}}},$$

Since, when $[H^+] = 1$, and $p_{H_2} = 1$, $E = 0$, by definition.

But, from (1) above,

$$\frac{[H^+]}{(p_{H_2})^{\frac{1}{2}}} = \frac{1}{K'}\,\frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Hence,
$$E = \frac{RT}{F}\log_e\frac{[Fe^{+++}]}{[Fe^{++}]} + K,$$

where K is a constant. It has the dimensions of a potential, and may be called E_o, so that

$$E = E_o + \frac{RT}{F}\log_e\frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Since, when $[Fe^{+++}] = [Fe^{++}] = 1$ (*i.e.*, in a solution normal with respect to both ions) the logarithmic term is zero, it follows that E_o is the normal electrode potential of the process

$$Fe^{+++} + \epsilon \longrightarrow Fe^{++},$$

and is therefore called the "oxidation potential" of that process.

In the general case, where the difference between the valencies is n, the equation is

$$E = E_o + \frac{RT}{nF}\log_e\frac{c_2}{c_1}.$$

Thus, in the case of tin, the process is

$$Sn^{++++} + 2\epsilon \longrightarrow Sn^{++},$$

and the equation governing it is

$$E = E_o + \frac{RT}{2F}\log\frac{c_2}{c_1}.$$

By measuring the voltages of cells made up, for example, as follows :—

Negative pole : Hydrogen electrode.

Positive pole: Platinum plate in a solution containing ferric and ferrous chlorides,

we can determine the oxidation potential of such reactions

$$Fe^{+++} + \epsilon \longrightarrow Fe^{++}.$$

The Table gives some of the values obtained for this and other similar reactions.

TABLE CVII.

Reaction.	Potential, volts.
$Co^{+++} \longrightarrow Co^{++}$	+ 1·82
$Pb^{++++} \longrightarrow Pb^{++}$	+ 1·80
$Ce^{++++} \longrightarrow Ce^{+++}$	+ 1·57
$Tl^{+++} \longrightarrow Tl^{+}$	+ 1·24
$Fe^{+++} \longrightarrow Fe^{++}$	+ 0·76
$Fe(CN)_6^{----} \longrightarrow Fe(CN)_6^{---}$	+ 0·41
$Cu^{++} \longrightarrow Cu^{+}$	+ 0·17
$Ti^{++++} \longrightarrow Ti^{+++}$	− 0·06
$V^{+++} \longrightarrow V^{++}$	− 0·2
$Cr^{+++} \longrightarrow Cr^{++}$	− 0·4

A positive sign means that a M solution of the ions is more easily reduced than a M solution of an acid is reduced to hydrogen.

What information can be gained from this table of oxidation-reduction potentials? Since the electrode $Fe^{+++} \longrightarrow Fe^{++}$ has a positive potential of 0·76 volt compared with the hydrogen electrode, it follows that it is capable of giving up electrons more easily than will the hydrogen of an acid. Hence, the solution of ferric salt may be reduced by hydrogen under atmospheric pressure. The electrode $Cr^{+++} \longrightarrow Cr^{++}$ possesses a negative potential of 0·4 volt. Hydrogen under atmospheric pressure cannot bring about this reduction, since a molar solution of Cr^{+++} ions is less easily reduced to Cr^{++} ions than a molar solution of H^{+} ions is reduced to H. In fact, when a chromous salt is oxidised by hydrogen ions to a chromic salt, hydrogen is evolved. Hydrogen is also liberated from aqueous solutions of vanadous salts, and of the bivalent compounds of tungsten and samarium, oxidation taking place.

The reducing or oxidising powers of metals in contact with certain ions can also be obtained by considering the electronegative series of the metals, and the list of oxidation reduction potentials together. Thus, copper with an electrode potential + 0·35 volt can reduce ferric salts, though with greater difficulty than hydrogen. Silver, however, with an electrode potential + 0·80 volt, being more positive than the $Fe^{+++} \longrightarrow Fe^{++}$ electrode, cannot bring about the reduction. Indeed, the reverse change will take place. Ferrous sulphate solution reduces silver nitrate to metallic silver.

Another method of representing the oxidising or reducing tendency of a system has been proposed. This is the r_H value. When a substance is an oxidising agent it *tends* to take up hydrogen; if it is a reducing agent it *tends* to evolve hydrogen. All oxidising and reducing actions are certainly not associated with the taking up or liberation of hydrogen, but they may, in effect, be regarded as such. The more a system tends to take up hydrogen, the greater is its oxidising power; the more it tends to evolve hydrogen, the greater is its reducing power. It follows that in a reversible oxidation-reduction system, such as

$$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++},$$

the pressure of hydrogen with which the system is *theoretically* in equilibrium (the p_{H_2} of equation (1), p. 645), is a measure of the reducing or oxidising power of the system. In very few cases can this hydrogen pressure be actually measured, as it is so small, but it may be calculated from electrochemical observations. The r_H *value for any system is the logarithm to the base* 10 *of the reciprocal of this hydrogen pressure, measured in atmospheres.* By comparing r_H values, it is possible to say whether one system will oxidise another or reduce it.

324. Applications of Electrochemistry.—(*a*) *To the Study of Chemical Affinity.*—This has already been referred to in a previous section (§ 320). The reversible e.m.f. of a cell is a measure of the free energy of the reaction going on in it. The validity of this method of determining affinity has been carefully tested by a number of observers, and particularly by Knüpffer and Bredig.

The chemical reaction

$$TlCl + KCNS = TlCNS + KCl$$

was carried out in a cell by means of the following arrangement.

Tl amalgam	KCNS solution saturated with TlCNS	KCl solution saturated with TlCl	Tl amalgam

The e.m.f. of the cell was determined at various temperatures, and the affinity calculated. If the electromotive force is a correct measure of affinity, then the equilibrium constants calculated from the van't Hoff isotherm should agree with those obtained by analytical methods. It is seen from the results given on p. 648 that this is the case.

This provides strong evidence for the validity of the electrochemical method of determining affinity.

The equilibrium constant, K, in the van't Hoff isotherm,

$$A = RT \log K - RT\Sigma n \log C$$

is a function of the temperature, so that it is possible, by varying

Temp.	*K*	
	Calc.	*Obs.* (analytical).
39·9° C.	0·88	0·85
20° C.	1·26	1·24
0·8° C.	1·79	1·74

the temperature, to make the second term of the equation equal to the first, when the affinity would be zero. At this temperature the electromotive force of the cell should be zero, if affinity is measured by this quantity. Knüpffer found that for the above cell the e.m.f. was zero at 42·3° C. This was the value found experimentally by altering the temperature of the cell until it gave no e.m.f. The temperature calculated from the isotherm was 41·3° C., again in good agreement.

There seems little doubt then that the electromotive force method does indeed give a correct result for the affinity of a chemical reaction.

(*b*) *To the Determination of the Solubility of a Sparingly Soluble Salt, and of Solubility Products.*—It is clear that the electromotive force of a concentration cell can be used to give the concentration of ions in a solution. For sparingly soluble substances the ionic concentration may be taken as the true solubility, the substance being supposed to be entirely dissociated. In this way the solubility of a sparingly soluble salt, such as silver chloride, can be determined with great accuracy.

Suppose that the following cell is set up :—

Ag |	$N/100AgNO_3$	Saturated NH_4NO_3	$N/10KCl$ saturated with AgCl	Ag

The current flows through the cell from the potassium chloride side to the silver nitrate side. The potassium chloride is added in order to make the cell conduct. The silver chloride itself furnishes so few ions that the cell would have a very high resistance if this were not done. The saturated ammonium nitrate solution which forms the bridge between the two silver solutions is used to make the e.m.f. between the two silver solutions negligible. If this were not used, a correction would have to be applied to eliminate the effect of the junction potential (p. 652). In the $N/10$ potassium chloride + silver chloride solution, the silver chloride gives rise to both silver and chlorine ions, but the concentration of chlorine ions from the silver chloride is negligible when compared with that from the potassium chloride.

Hence, assuming that the potassium chloride is completely dissociated, the concentration of chlorine ions is 0·1.

If S is the solubility product, then

$$S = [Ag^+][Cl^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The solubility, M, $= \sqrt{S} = \sqrt{[Ag^+][Cl^-]}$

But $[Cl^-] = 0{\cdot}1$, so that $M = \sqrt{[Ag^+]0{\cdot}1}$ . . . . (2)

The value of $[Ag^+]$ can be determined from the e.m.f. of the cell. If the e.m.f. is E, we have

$$E = \frac{RT}{nF} \log_e \frac{0{\cdot}01}{c},$$

where c is the concentration in gram-equivalents per litre of Ag^+ ions required. Substituting for R, T, n, F, and bringing to common logarithms, the equation becomes

$$E = 0{\cdot}058 \log_{10} \frac{0{\cdot}01}{c},$$

where E is the e.m.f. in volts.

From this c can be calculated and substituted in equation (1), from which the solubility product can be obtained. The solubility can then be calculated.

A cell of a slightly different type has been used by Goodwin for the determination of the solubility of silver chloride. This cell involves the use of a chlorine electrode (*i.e.*, a platinum foil, surrounded by chlorine), and is represented as follows :—

$$Ag \mid N/10KCl \text{ saturated with } AgCl \mid Cl$$

Since the chlorine electrode produces anions, the e.m.f. of the cell is not the difference between the two electrode potentials, but the sum of them. Thus we have for the e.m.f.

$$E = 0{\cdot}058 \log \frac{[Ag^+]}{[Ag]} + 0{\cdot}058 \log \frac{[Cl^-]}{[Cl]}.$$

Now, $-0{\cdot}058 \log [Ag]$ and $-0{\cdot}058 \log [Cl]$ are merely the electrode potentials of Ag and Cl respectively, and are known. The e.m.f., E, is determined, and $[Cl^-]$ is known (0·1). Hence, $[Ag^+]$ can be calculated, and the solubility product obtained as before.

(c) *To the Determination of Valency.*—The expression for the e.m.f.

$$E_1 - E_2 = \frac{RT}{nF} \log_e \frac{c_1}{c_2}$$

involves the valency of the ions, n. If, therefore, we know, or can determine, the values of the other quantities in the expression, n can be obtained.

The best example of the use of this method for finding valency is the work of Ogg on the valency of the mercurous ion. If the cell

Hg	$N/2$ mercurous nitrate in $N/10$ nitric acid	$N/20$ mercurous nitrate in $N/10$ nitric acid
+		

is set up, and its e.m.f. determined, n can be found by the following calculation. Let the concentration of mercury ions in the $N/20$ solution be c_1, and that in the $N/2$ solution c_2. If the liquid/liquid potential is neglected, we have

$$-E = \frac{RT}{nF}\log_e\frac{c_2}{c_1} = \frac{0{\cdot}058}{n}\log_{10}\frac{c_2}{c_1},$$

where E is the e.m.f. of the cell. If it is supposed that the solutions are completely dissociated (which is, of course, only true to a first approximation), we have

$$\frac{c_2}{c_1} = \frac{20}{2} = 10.$$

Ogg found the potential of the cell to be 0·029 volt. Hence,

$$0{\cdot}029 = \frac{0{\cdot}058}{n}, \quad \therefore n = 2.$$

Thus, the valency of the mercurous ion is 2, and it should be represented as Hg_2^{++}, the formula of a mercurous salt, say the nitrate, being $Hg_2(NO_3)_2$. There are many other pieces of evidence which point to the same conclusion. The depression of the freezing point of dilute solutions of nitric acid when mercurous nitrate is dissolved in them provides evidence for the existence of Hg_2^{++} ions.

(*d*) *To the Determination of the Degree of Hydrolysis of Salts.*—This has been briefly mentioned in Chapter XIII., § 282. The method consists in determining the hydrogen ion concentration in a solution of the salt. The cell used is made up of a hydrogen electrode in the solution of the salt under investigation and a calomel electrode. The two are separated by a bridge solution of ammonium nitrate to nullify the liquid/liquid potential.

The advantage of this method is that it is applicable in those cases where the p_H is small, In fact, it works better for small hydrogen ion concentrations than for large. Other methods are just the reverse. The disadvantages, however, are that it cannot be used in the presence of salts of elements which would be deposited on the platinum electrode, nor in the presence of reducible cations or anions, such as Fe^{+++} or NO_3^-. It has, however, been used satisfactorily for the determination of the degree of hydrolysis of such salts as aluminium and nickel chlorides.

The standard case dealt with in the laboratory by this method is

the determination of the degree of hydrolysis of aniline hydrochloride. This hydrolyses according to the equation

$$C_6H_5NH_2 . HCl + H_2O = C_6H_5 . NH_3OH + HCl.$$

Suppose the following cell is made up

H_2	$N/32\ C_6H_5NH_2HCl$	Saturated NH_4NO_3	Normal KCl saturated with Hg_2Cl_2	Hg

The single potential at the hydrogen electrode is

$$\pi = \frac{RT}{nF} \log \frac{[H^+]}{C},$$

where $[H^+]$ is the concentration of hydrogen ions in the solution and C is the pressure of hydrogen gas. But $-RT \log C$ is the electrode potential of the normal hydrogen electrode, which is known from other measurements, and can be called π_0. Thus,

$$\pi = \pi_0 + \frac{RT}{nF} \log [H^+].$$

Considering the equilibrium in the hydrolysis, if we have one gram-molecule of the salt dissolved in v litres of water, and a fraction x is hydrolysed, then we have for the hydrolysis constant, K,

$$K = \frac{x^2}{(1-x)v}.$$

But the concentration of hydrogen ions is x/v, assuming the acid formed to be completely dissociated. Hence, the equation for the single potential becomes

$$\pi = \pi_0 + \frac{RT}{nF} \log \frac{x}{v}.$$

The argument is best followed by taking a definite example. When dealing with $N/32$ aniline hydrochloride, the e.m.f. of the cell set up was 0·4655 volt. The normal calomel electrode has an absolute potential of + 0·56 volt. Hence, the p.d. of the hydrogen electrode must be 0·56 − 0·4655 = + 0·0945 volt. We have then

$$0{\cdot}0945 = \pi_0 + \frac{RT}{nF} \log \frac{x}{v}.$$

The absolute electrode potential of hydrogen, π_0, is 0·0277 volt. Thus, converting to common logarithms, and substituting for R, T (25° C.) and F, we have

$$0{\cdot}058 \log_{10} \frac{x}{v} = 0{\cdot}0945 - 0{\cdot}277 = -0{\cdot}1825,$$

$$\therefore \frac{x}{v} = 0{\cdot}000807.$$

If the aniline hydrochloride were completely dissociated, the concentration of hydrogen ions would be 0·03125. The actual concentration is 0·000807. Hence, the percentage hydrolysis is

$$\frac{0{\cdot}000807}{0{\cdot}03125} \times 100 = 2{\cdot}58,$$

and the hydrolysis constant is

$$K = \frac{(0{\cdot}000807)^2}{32(1 - 0{\cdot}000807)} = 0{\cdot}000021.$$

(*e*) *To the Determination of Transport Numbers.*—We have not yet investigated the liquid/liquid potential in a cell. In the derivation of the formula (§ 277), it will be remembered, this potential was neglected, and then, in order to make this assumption correct practically, a bridge solution of ammonium nitrate was introduced into the cells. The reason for the liquid/liquid potential is that there is a transference of ions unequally, due to the differing mobilities of the ions. In the derivation of the formula (§ 277), it was assumed that when a Faraday of electricity passed through the cell, the effect would be to add one gram-ion to the anode compartment of the cell, and remove one gram-ion from the cathode compartment. This is not what happens, because the ions have different mobilities. Consider the cell

$$\begin{array}{cccc} & & -|+ & & \\ & HCl & & HCl & \\ H_2 & & & & H_2 \\ & c_1 & & c_2 & \\ & \text{(conc.)} & & \text{(dilute)} & \end{array}$$

Suppose that c_1 is greater than c_2. Then osmotic pressure tends to make the hydrochloric acid diffuse from the concentrated to the dilute solution. The hydrogen ion H^+ has a greater mobility than the chlorine ion Cl^-, and tends to outstrip it, giving rise to an e.m.f. at the junction such as to slow up the hydrogen ions, and hasten the chlorine ions, till both diffuse across at the same rate, as they must. Thus, the dilute solution (c_2) becomes positive relative to the concentrated solution (c_1). Let the liquid/liquid potential be $E_{liq.}$. When one Faraday of electricity passes through the cell, m_a gram-equivalents of Cl^- pass across the boundary in the one direction and m_c gram-equivalents of H^+ pass across in the other. The respective amounts of work done are :—

$$m_a F E_{liq.} = m_a RT \log_e \frac{c_2}{c_1},$$

and

$$m_c F E_{liq.} = m_c RT \log_e \frac{c_1}{c_2}.$$

assuming that the acid is 100 per cent. ionised. In our case, $m_c > m_a$.

Adding, and remembering that $m_c + m_a = 1$, we have,

$$FE_{\text{liq}} = (m_c - m_a)\,RT \log_e \frac{c_1}{c_2};$$

i.e.,
$$E_{\text{liq}} = (m_c - m_a)\,\frac{RT}{F} \log_e \frac{c_1}{c_2},$$

directed from c_2 to c_1.

Taking no account of the liquid/liquid potential, the e.m.f. of the concentration cell is given by

$$E = \frac{RT}{F} \log_e \frac{c_1}{c_2} = (m_c + m_a)\,\frac{RT}{F} \log_e \frac{c_1}{c_2},$$

directed from c_1 towards c_2.

To obtain the total potential, E_T, we form the *algebraic* sum of E, and $E_{\text{liq.}}$, *i.e.*,

$$E_T = \left[\frac{RT}{F} \log_e \frac{c_1}{c_2}\right] [m_c + m_a - (m_c - m_a)],$$
$$= 2m_a \,.\, \frac{RT}{F} \,.\, \log_e \frac{c_1}{c_2},$$

directed from c_1 towards c_2.

This equation involves the transport number of the anion, and can be made use of to determine this constant. A double cell (or "concentration cell without transport") is arranged as follows:—

Hg	NKCl saturated with Hg_2Cl_2	Saturated NH_4NO_3	HCl conc. c_1	H – H	HCl conc. c_2	Saturated NH_4NO_3	NKCl saturated with Hg_2Cl_2	Hg

If the hydrogen chloride is supposed to be completely dissociated, the e.m.f. of this cell, with the bridge solutions, is

$$E_1 = \frac{RT}{nF} \log_e \frac{c_1}{c_2},$$

since the two calomel electrodes exert an equal and opposite effect on the potential, and the system reduces to a hydrogen concentration cell without the liquid/liquid potential. If no bridge solutions are used, the different concentrations c_1 and c_2 of the acid affect the partial potentials at the hydrogen electrodes, and also the partial potentials of the calomel electrodes. These two effects are equal, and add together, giving for the e.m.f. of the cell *without bridge solutions*

$$E_1' = \frac{2RT}{nF} \log_e \frac{c_1}{c_2}.$$

The e.m.f. of a single hydrochloric acid concentration cell, consisting of two hydrogen electrodes dipping into acid of concentrations c_1 and c_2 (concentration cell with transport), would be

$$E_2 = \frac{2m_a RT}{nF} \log_e \frac{c_1}{c_2}.$$

If E_1 (or E_1') and E_2 are measured, it is clear that m_a can be calculated. The transport number of the cation, m_c, is equal to $1 - m_a$. This method yields results which are in excellent agreement with those determined by the usual Hittorf apparatus.

(*f*) *To the Study of Allotropy.*—If there are two forms of the same element, there will be a potential difference between them when placed in a solution containing ions of the element. Thus, tin exists in two forms, white and grey. The change from the one to the other is a very slow process at ordinary temperatures. In order to determine the transition point, Cohen prepared a cell with ammonium stannichloride, $(NH_4)_2SnCl_6$, as electrolyte, and white and grey tin as the electrodes. The temperature of the cell was then altered, and it was found that at 18° C. the cell gave no e.m.f. This temperature must be that at which the two forms are equally stable, *i.e.*, the transition temperature.

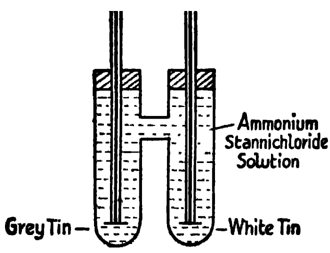


FIG. 193.
Cell for studying Allotropy of Tin.

A similar method can be used for determining the transition points of salt hydrates. Thus, to determine the transition point of the change of zinc sulphate heptahydrate into zinc sulphate hexahydrate a cell is prepared as shown in Fig. 194. The limb A contains a saturated solution of the heptahydrate and some of the solid salt. B contains a saturated solution of the hexahydrate together with some of the salt. The tube C, which links the two, is bent downwards to prevent the mixing of the solutions by convection currents. Two zinc electrodes go to the bottoms of tubes A and B. The cell is placed in a thermostat and connected with a galvanometer. At temperatures below the transition point the solubility of the hexahydrate, which is the metastable form, will be greater than that of the heptahydrate (§ 133). Hence, a current will flow outside the cell, from the electrode in the hexahydrate solution to that in the heptahydrate. At the transition point the solubilities become equal and the cell then gives no e.m.f. At temperatures slightly above the transition point the direction of flow of the current is

reversed. By noting the temperature at which the cell gives no e.m.f., *i.e.*, when there is no deflection of the galvanometer on completing the circuit, the transition point is obtained to a high degree of accuracy.

In the example given, the electrodes consisted of the same metal as the ions in the solution, but in some cases this cannot be arranged, and, in fact, it is not always necessary. For example, to determine the transition point of sodium sulphate decahydrate, it is convenient to use a suitable non-polarisable mercury electrode.

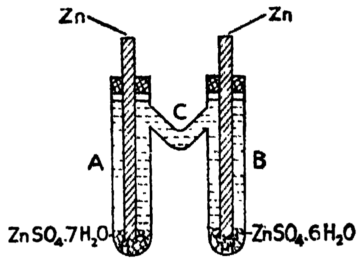


FIG. 194.—Cell for determining Transition Point of Hydrate of Zinc Sulphate.

(*g*) *To the Study of Complex Ions.*—By means of a concentration cell it is possible to determine the concentration of ions in a solution of a complex salt. For example, the concentration of silver ions in a solution of a complex silver salt, say diamminoargentic nitrate, can be found by preparing the cell

$$\mathrm{Ag} \mid \text{Ammoniacal soln. of } \mathrm{Ag_2O}^{1} \mid \frac{N}{10}\,\mathrm{AgNO_3} \mid \mathrm{Ag}$$

and determining its e.m.f. In this way the degree of dissociation of the complex ion and its instability constant can be found. The stability of the complex $[Ag(CN)_3]^{--}$ can be found by determining the e.m.f. of the cell

$$\mathrm{Ag} \mid \frac{N}{10}\,\mathrm{AgNO_3} \mid \mathrm{KNO_3} \quad \frac{N}{20}\,\mathrm{K_2[Ag(CN)_3]} \; \frac{N}{10}\,\mathrm{KCN} \mid \mathrm{Ag}$$

The instability constant k is $\dfrac{[Ag^+]\,[CN^-]^3}{[Ag(CN)_3]^-}$

and can be found from the data arrived at experimentally.

There is little difference between a complex salt like potassium ferrocyanide and a double salt like ferrous ammonium sulphate. The classification of a salt into one or other of these classes can usually be made by considering its stability constant. Thus, potassium ferrocyanide gives rise to a complex ion, $[Fe(CN)_6]^{----}$, which is very stable, whilst ferrous ammonium sulphate gives rise to a complex ion, $[Fe(SO_4)_2]^{--}$, which is very unstable. The e.m.f. method thus allows one to find the stability of the complex ion, and enables a classification to be made; although, even so, this is a

[1] Made by adding ammonium hydroxide to silver nitrate solution.

matter of some difficulty, as ions are known of all stabilities from that of the ferrocyanide ion to that of the ferrosulphate ion, and it is difficult to draw the line between the two classes (§ 298).

(*h*) *Potentiometric Titration.*—This has already been mentioned in § 287.

325. Polarisation.—When a voltaic cell, consisting of a zinc and a copper plate in dilute sulphuric acid, is set up and a current is taken from it, the e.m.f. of the cell rapidly falls. This is because the electrodes become covered with bubbles of gas, which make gas electrodes with e.m.f.'s opposite to that of the cell. If the bubbles of gas are removed, mechanically or chemically, the e.m.f. of the cell remains constant. This phenomenon of a reverse e.m.f. brought about by the presence of the products of electrolysis is called *polarisation*. For a given concentration of electrolyte, the polarisation e.m.f. for any given type of cell is constant. Of course, exactly the same phenomenon is met with in electrolysis, in which the reactions are just the reverse of those taking place in a cell. Thus, if dilute sulphuric acid is electrolysed between platinum electrodes, a certain minimum e.m.f. must be applied to the electrodes to bring about continuous electrolysis. At first, a very small e.m.f. will bring about electrolysis, but almost immediately the electrodes become coated with bubbles of gas which exert an opposing effect, and, unless the applied e.m.f. is greater than the polarisation e.m.f., electrolysis almost stops. A slight current flows when the electrolysing e.m.f. is less than the opposing polarisation e.m.f., owing to diffusion of the gases away from the electrodes.

This polarisation may also be brought about by changes in concentration of the electrolyte. If a solution of copper sulphate is electrolysed between copper electrodes, at first a very small e.m.f. will suffice to cause electrolysis; but, after a while, the concentration of copper sulphate in the neighbourhood of the anode and cathode respectively, alters, owing to the different transport numbers of the copper and sulphate ions. Thus a concentration cell is set up, the e.m.f. of which opposes the electrolysing e.m.f.

The minimum voltage required for appreciable electrolysis is called the *decomposition potential*. This will vary from metal to metal. The value of the decomposition potential clearly depends on the electrode potential of the electrode in contact with the solution of its salt. This fact is made use of in depositing metals from solutions in which they are mixed. Thus copper and zinc may be separated electrolytically. The decomposition potential of copper sulphate is 1·49 volts, and of zinc sulphate 2·55 volts, using electrodes of copper and of zinc respectively. If copper plates are used as electrodes in the electrolysis of this solution,

copper only will be deposited if the electrolysing potential is less than about 2·5 volts.

326. Hydrogen Overvoltage.—Theoretically, since the electrode potential of lead is $-0{\cdot}12$ volt, when an acid solution of a lead salt is electrolysed between lead electrodes, hydrogen should be liberated at the cathode, and no lead. Actually, however, lead is deposited (cf. the lead accumulator). This is because most metallic electrodes have to be raised to a higher potential than that indicated in the electronegative series in order to enable hydrogen to be liberated. This additional voltage is known as *hydrogen overvoltage.* It varies from metal to metal.

The existence of overvoltage explains numerous phenomena. In the first place, it explains why the lead accumulator is a practical piece of apparatus. If it were not for the considerable overvoltage of this metal, lead would not be deposited on the negative plate when the cell was charged. If the lead is covered with a layer of a metal with a very low overvoltage, *e.g.*, platinum, and the electrolysis is carried out, no lead is deposited, but hydrogen is liberated.

Overvoltage is made use of in many electrolytic processes. If electrodes with high overvoltages are used in electrolytic reductions it amounts to the same thing as enhancing the activity of the hydrogen. It is for this reason that lead electrodes are frequently used instead of platinum in some organic electrolytic reductions (*e.g.*, the reduction of nitrobenzene).

Although a great deal of research has been carried out on overvoltage, no satisfactory explanation of the phenomenon has yet been offered.

Overvoltage occurs also at electrodes at which gases other than hydrogen are evolved.

SUMMARY

The First Law of Thermodynamics states that mechanical energy and heat energy are quantitatively interconvertible.

In any system, if the decrease in the internal energy is U, the free energy (*i.e.*, energy used in performing external work) is A, and the heat tonality is Q

$$U = A - Q.$$

When Q is positive, heat is taken in by the system. When it is negative, heat is given out.

The Second Law of Thermodynamics states that heat cannot of itself pass from a colder to a warmer body.

The maximum amount of work which can be done by a physical or chemical change is only obtained when the change takes place reversibly (in the thermodynamic sense).

The affinity of a chemical reaction is measured by the amount of

free energy (A) available. It is the maximum external work that the reaction may be made to perform.

The affinity of a chemical reaction may be obtained (1) by the use of the Gibbs-Helmholtz equation, $A = U + T\frac{dA}{dT}$, where A is the affinity, U the diminution in internal energy, and T the absolute temperature; (2) from equilibrium constants, using the van't Hoff isotherm; (3) by applying the Nernst Heat Theorem.

When a metal plate is placed in a solution of one of its salts it becomes charged to a definite potential owing to the tendency for it to pass into solution. This potential, which is referred to that on a platinum foil in the presence of hydrogen gas, dipping into a normal solution of an acid (the normal hydrogen electrode) as zero, is called the "electrode potential." It varies from metal to metal. By studying cells made up of combinations of electrodes much valuable information can be obtained concerning chemical affinity, solubilities of sparingly soluble salts, valency, the nature of complex ions, transport numbers of ions, degree of hydrolysis of salts, allotropy, etc.

The deposition of one metal from a solution of its salt by another metal depends upon the position of the metals in the series of electrode potentials.

SUGGESTIONS FOR FURTHER READING

HINSHELWOOD, C. N. "Thermodynamics." (*Methuen*, 1926.)
PARTINGTON, J. R. "Thermodynamics." (*Constable*, 1913.)

QUESTIONS

(1) What do you understand by a reversible process in the thermodynamic sense? Describe one reversible process, evaluating the energy changes at each step.

(2) What do you understand by chemical affinity? How would you measure the affinity of a reaction?

(3) It was the custom to talk of the affinity of one substance for another. Is it still possible to use these terms?

(4) Derive the formula for the e.m.f. of a concentration cell without transport. Note carefully the approximations made. How do these affect the result?

(5) What physico-chemical information can be derived from measurements of the e.m.f. of cells?

(6) How would you determine the solubility product of silver chloride?

(7) Of what interest is a table of oxidation-reduction potentials?

CHAPTER XVII

COLLOIDS AND SURFACE PHENOMENA

327. General.—An ordinary solution consists of a solvent and a solute. The solute is molecularly dispersed in the solvent, *i.e.*, the substance is broken down completely to molecules (and, in some cases, still further to ions). In a colloidal solution, the substance corresponding to the solute in an ordinary solution is not molecularly dispersed, but exists in aggregates of some hundreds or thousands of molecules, in the "solvent" (better termed, in this case, the "dispersion medium").

A colloidal solution cannot always be distinguished from a true solution with the naked eye. The particles, even though they may consist of some thousands of molecules, will pass through a filter paper, and cannot be seen under the microscope. A colloidal solution, however, is a two-phase system, whereas a true solution is regarded as being homogeneous, and therefore consists of only one phase.

Since the vast majority of substances have been obtained in colloidal solution, it is now customary to use the word "colloid" to represent a state of matter.

328. Historical Development of Colloid Chemistry.—Graham is usually regarded as the founder of the science of colloids. He certainly laid the foundation of the more serious study of the subject by his researches on liquid diffusion (1851–61), but many of the phenomena he noted and that have been noted since were well known very early in the history of chemistry.

Colloidal solutions of metals were fairly well known at Graham's time. The method of obtaining colloidal gold by reduction of gold salts with tin solutions was known as early as 1685. Berzelius was acquainted with a number of colloidal solutions. He refers to colloidal arsenious sulphide in the words: "For the present this solution is rather to be regarded as a suspension of transparent particles, for arsenious sulphide gradually separates out as a precipitate." He also knew of colloidal silica, which he obtained by the hydrolysis of silicon sulphide. "β-silicic acid is obtained in its purest form when silicon sulphide is oxidised by water: hydrogen sulphide is evolved as a gas, and the β-silicic acid dissolves in the

water. In a more concentrated state the solution soon turns to a gelatinous mass." Sobrero and Selmi, in 1850, gave an elaborate account of the preparation of colloidal sulphur, though, of course, it was not known by that name.

The researches of Graham occupied a number of years, his first paper on the subject appearing in 1851, whilst the last was published in 1861. Graham compared the rates of diffusion of a large number of substances, both inorganic and organic, and considered that liquid diffusion could be compared to volatility. He says, "the range in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions." Certain substances, whilst varying among themselves in diffusibility, agree in diffusing much more rapidly than substances falling into another class, and they are therefore the "volatile" substances. These are salts and normal liquids. The other much more difficultly diffusible class comprises substances which are difficult to crystallise, such as starch, gum, tannin, albumen, gelatine, and glue. Graham called the first class *crystalloids* and the second *colloids*, from the Greek word *Kolla*, meaning "glue."

The difference between the classes was not very definite. Many substances appeared to be on the borderline. Nevertheless, the classification served a very useful purpose in chemistry.

329. General Nature of Colloids.—Crystalloids are capable of diffusing through a colloidal membrane, such as parchment, almost as quickly as they can diffuse through water, whilst colloids are remarkable in being unable to diffuse through such membranes. This fact was noted by Graham, who said that "of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids."

This property is made use of in dialysis, a process used in the purification of colloidal solutions and which will be further referred to later (§ 331).

Graham also noted that "solutions" of substances which were normally insoluble in water could be obtained (p. 665), and that these behaved just like the colloids in many respects. They behaved similarly on dialysis, and often could be set to a jelly or coagulated by adding a salt. He used the term "sol" for a colloidal solution, and the word "gel" for the products of coagulation.

Ostwald regarded colloidal solutions as essentially heterogeneous systems, consisting of two phases, a disperse phase, which consisted of the colloidal particles, whilst the other was the dispersion medium. A colloidal solution of silver in water consisted of a disperse phase (the very finely divided silver), and the dispersion medium (water).

Colloidal solutions cannot be regarded as an entirely new section of the whole range of solution. Actually they are intermediate between solutions and precipitates, and there is a gradual transition between the two. Colloidal particles may be fairly large, bordering on being a precipitate, whilst they may be very small, bordering on true solution. It is usual to measure the diameter of colloidal particles in $m\mu$.[1] 1 μ is 10^{-4} cm., and 1 $m\mu$ is 10^{-7} cm. Colloidal particles may be from 1 to 100 $m\mu$ in diameter. Above the latter they are suspensions, and below the former they cannot be distinguished from true solutions.

The degree of dispersion, then, is the characteristic that marks out the colloid. Von Weimarn has shown that the degree of dispersion of a precipitate can be varied at will by correct choice of the concentrations of reacting solutions. In this way it is possible to make any precipitate into a colloidal solution. The relationship obtained by von Weimarn is

$$\delta = \frac{C}{S}\eta$$

δ being the fineness of the particles (smaller the larger the particles), S the solubility of the slightly soluble substance, C is the state of supersaturation that would have been reached if the substance had not come out of solution, and η is the coefficient of viscosity of the solution. The work of von Weimarn indicates that it is possible to obtain in the colloidal state any substance which normally is precipitated, and shows that the difference between colloidal and ordinary solutions is one of degree only.

The truth of this statement may be easily tested with the well-known barium sulphate precipitate. If barium sulphate is precipitated in the cold, it is found to be very difficult to filter; the particles are so small that they pass through a filter paper (a filter paper will usually retain particles as small as 5,000 $m\mu$). If the barium sulphate is prepared hot, it is much more easy to filter it cleanly, because now the particles are larger in size. The reason for this is that at the higher temperature the solubility of the barium sulphate is greater and the viscosity of the water less, making δ smaller. It is even possible to obtain a barium sulphate gel. Von Weimarn states that any very difficultly soluble salt will separate as a gel if made by mixing sufficiently concentrated solutions, and recommends for the preparation of barium sulphate in this state the mixing of $3N$ aqueous solutions of barium thiocyanate and manganous sulphate. On long standing the gel takes up the ordinary form again.

[1] The term $\mu\mu$ may sometimes be met instead of $m\mu$, but the latter is the form sanctioned by the Chemical Society.

A similar experiment may be tried with calcium acetate in alcohol. Calcium acetate is somewhat soluble in alcohol, but can be obtained in the form of a gel by suddenly making a supersaturated solution of it in alcohol. This is done by making a saturated aqueous solution of calcium acetate. 10 C.c. of this solution are taken and mixed by tossing from one beaker to another and back again, with 90 c.c. of 95 per cent. alcohol. A jelly sets at once. Acetone may be substituted for alcohol. For the success of this experiment it is absolutely necessary to have the aqueous solution of calcium acetate saturated. This process is one of those used for manufacturing solidified alcohol, employed as a patent fuel.

330. Classification of Colloids.—Colloidal solutions are referred to as *sols*. If the dispersion medium is water, they are called "hydrosols," or sometimes "aquasols." If alcohol is the dispersion medium, the colloidal solution is called an "alcosol."

Strong solutions of certain colloids set to a jelly. This is called a *gel*.

Sols are frequently subdivided into lyophobic (solvent-hating) and lyophilic (solvent-loving) colloids. The first class includes those sols which are readily precipitated from solution, and which then do not pass back into colloidal solution on addition of the dispersion medium. Thus a silver sol, once coagulated, cannot be made to revert to the colloidal state merely by the addition of the dispersion medium. It can, however, be re-obtained in colloidal solution by the process of peptisation (§ 332). The lyophobic sols are sometimes called also "irreversible sols." On the other hand, the lyophilic sols are reversible. Gelatin, gum arabic, and starch are colloids of this type. They are much more stable than lyophobic sols, and are not, therefore, easily precipitated. They will easily revert to the colloidal state after precipitation, on adding the dispersion medium.

Ostwald[1] drew up a list of all the possible colloidal solutions, which is embodied in Table CVIII.

It has already been stated that a colloidal solution containing separate particles, such as a colloidal solution of gold or silver, is called a sol. In addition to the classification into lyophilic and lyophobic sols, true colloidal solutions may be divided into two classes, (*a*) colloidal electrolytes, and (*b*) non-electrolytic colloidal solutions.

The class of colloidal electrolytes is very interesting, and may be best illustrated by considering the soaps. If one of the higher fatty acids, such as palmitic acid, is added to water it will form a very thin film on the surface of the water. The carboxyl group has an affinity for water, and is called "hydrophilic," whereas the hydro-

[1] Wolfgang Ostwald, son of Wilhelm Ostwald (who propounded the Dilution Law, etc.).

TABLE CVIII.—COLLOIDAL DISPERSIONS (OSTWALD)

Dispersion Medium.	Disperse Phase.	Name.
Gas.	Gas.	No colloidal dispersion. Perfect mixture always.
	Liquid.	Fog (cloud, mist) } aerosols.
	Solid.	Smoke } aerosols.
Liquid.	Gas.	Foam
	Liquid.	Emulsion } sols.
	Solid.	Colloidal suspension } sols.
Solid.	Gas.	Solid foam.
	Liquid.	Colloidally dispersed crystal inclusions. Solid emulsion.
	Solid.	Colloidally dispersed eutectics. Solid sols.

carbon residue attached to it is said to be "hydrophobic," since it has no affinity for water and tends to separate itself from it. The molecules will therefore orient themselves on the surface with the carboxyl groups in the water and the hydrocarbon residues sticking out from it.

If, now, caustic soda is added, a sodium salt—a soap—is formed. Palmitic acid is not dissociated to any extent, whereas the sodium salt is. The sodium ions are pulled into the water and escape, and the attraction of the sodium ions for the palmitate ions pulls the latter so strongly that they cannot remain on the surface, but are pulled beneath. They do not, however, lose their oily nature entirely, but form oily aggregates, each of which is called an "ionic micelle." Thus, we have a colloidal solution containing sodium ions in true solution, and aggregates of palmitate ions. This is known as a colloidal electrolyte. Colloidal solutions of such substances are easily made. No special process is necessary, since the solvent itself causes the dispersion.

Many dyes are colloidal in nature, and frequently behave as colloidal electrolytes, being dragged into colloidal solution by some powerfully ionised part of the molecule.

331. **Dialysis.**—The observation of Graham that colloids were unable to pass through a colloidal membrane, is made use of in separating a colloid from a crystalloid. It must be emphasised that the membrane used in dialysis is quite distinct in its properties

from the semi-permeable membrane used in experiments on osmotic pressure. The ordinary dialyser consists of a vessel open at both ends; one end can be covered by a parchment paper. A suitable vessel can be made by removing the bottom from a wide-mouthed bottle by means of a hot wire. The parchment should be moistened before being tied to the vessel. The dialyser is nearly filled with the colloidal solution and suspended in a vessel containing distilled water. The crystalloid gets through, leaving the colloid behind.

A suitable dialyser is also easily made entirely of parchment by

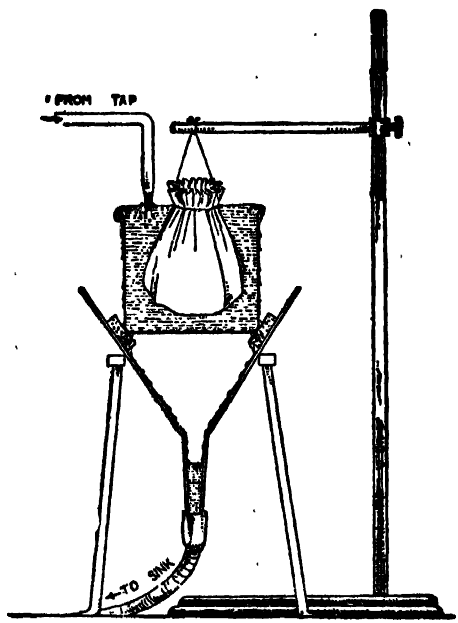


FIG. 195.—Dialyser.

folding a moistened sheet of it round a bottle and allowing to dry. The parchment bottle will be found to retain its shape. A cord can be tied round it, and when filled with colloidal solution it may then be suspended in distilled water by means of the cord. A simple form of dialyser can be prepared by making a purse-like bag of parchment paper and suspending it as shown in Fig. 195.

Many other membranes are suitable. Recently the use of cellophane has been advocated. Collodion dialysers are also readily made by taking a test-tube and dipping it in collodion solution and allowing it to dry. The skin of collodion can then be slipped off. It is better to take a Soxhlet extraction thimble and warm it with

warm water, leaving no excess. Then pour into it some collodion solution. Pour it out again and allow to dry. Then repeat to get a second layer.

Membranes of cellulose acetate have been used satisfactorily.

An interesting experiment on dialysis can be carried out by making a thin starch paste and putting it in a dialyser. Test the dialysate for glucose by means of Fehling's solution, and for starch by means of iodine. Now add to the starch some diastase and continue to test from time to time for glucose and starch in the dialysate. The action of the diastase converts the starch into a crystalloid—glucose, which will now come through the dialyser.

332. Peptisation.—If freshly prepared ferric hydroxide is treated with a small quantity of ferric chloride solution, it immediately forms a colloidal solution of a dark reddish-brown colour. The ferric chloride which has caused this dispersion is called a "peptising agent" and the process is called "peptisation." If all the ferric chloride is removed, the sol precipitates.

A similar colloidal solution is obtained with aluminium hydroxide by adding very dilute hydrochloric acid to the freshly prepared hydroxide. The amount of acid added is quite insufficient to form aluminium chloride. Stannic hydroxide sol is easily prepared by the addition of a solution of sodium stannate to one of sodium bicarbonate, washing the precipitate and suspending it in water, and then adding a small amount of ammonia.

In all these cases an electrolyte is necessary for the formation of the colloidal solution, and the stability of the substance depends on the adsorption of ions at the surface of the colloidal particles. If these are thoroughly washed with distilled water, the electrolyte can be removed and precipitation ensues. A lyophobic sol may be brought back into solution after coagulation by the process of peptisation (§ 330).

It may be mentioned that the reverse behaviour is sometimes met with. Washing a precipitate repeatedly with distilled water sometimes brings it into colloidal solution. An example is the formation of vanadic acid sols (p. 668).

The behaviour of colloidal solutions with electrolytes should be compared with peptisation (§ 339).

333. Preparation of Colloidal Solutions.—Many organic substances such as gum arabic, gelatin, starch, etc., form colloidal solutions merely on dissolving in water. These are the lyophilic colloids (§ 330). The same is true of colloidal electrolytes, such as the soaps, and some dyestuffs.

There are two general methods of making lyophobic sols. The first is the condensation method, in which molecularly dispersed

particles are built up. The second is the reduction method, in which material in the mass is broken down into colloidal particles.

In describing the various methods under each class, experimental details will be given of the methods of preparation of certain common colloidal solutions, and the student is recommended to carry these out practically, if possible.

In the preparation of colloidal solutions it is necessary that all vessels used should be thoroughly clean, and that the materials used should be pure. It will be shown later that precipitation of a colloid is readily occasioned by addition of an electrolyte (§ 339). Hence the necessity of using materials which are known to be pure. The thorough cleansing of vessels is best carried out by steaming them out.

I. *Condensation Methods*.—(*a*) *Reduction*.—This is the usual method for preparing colloidal metals. An example is the formation of colloidal gold, or silver, by reducing a solution of a salt of the metal, much diluted, with a reducing agent, usually organic, since these do not produce ions which are inimical to colloid formation.

Zsigmondy prepared colloidal gold by first making a solution of chlorauric acid, $HAuCl_4 . 3H_2O$, containing 6 gms. per litre, and also a solution of potassium carbonate, 0·18 normal. 1,200 C.c. of twice distilled water were heated, and 2·5 c.c. of the gold solution, and then 3·5 c.c. of the potassium carbonate solution were added. The mixture was stirred and heated to 100° C. It was removed from the source of heat, and 1·0–3·0 c.c. of 0·3 per cent. formaldehyde added with stirring. A gold sol was thus produced.

Von Weimarn used Rochelle salt for reducing gold chloride. 30 c.c. of 0·1 per cent. gold chloride solution were added to 400 c.c. of boiling water. Then about 2 c.c. of 0·05 *M* Rochelle salt were added drop by drop. The boiling was continued, and after about one minute blue gold appeared, which afterwards changed to red.

Ostwald reduced gold chloride with tannin and obtained a good red gold solution. To 100 c.c. of distilled water a few drops of 0·1 per cent. gold chloride solution were added, the latter having been carefully neutralised with the calculated amount of potassium carbonate. A few drops of a 0·1 per cent. solution of tannin were added. On warming, a cherry-red colour appeared, which could be deepened by adding more gold chloride and tannin. Tannin has some protective action (see Protection of Colloids, p. 686) and therefore the colloid will remain suspended longer than some others, especially if a few drops of chloroform are added to prevent the growth of mould.

Colloidal silver may be prepared as follows: To 5 c.c. of 1 per cent. silver nitrate solution, very dilute ammonia is added drop by drop

until the precipitate just disappears. Dilute to 100 c.c., mix with 0·4 c.c. of a 0·5 per cent. solution of tannin. By varying the proportions and the temperature at which the mixing is carried out, sols of various colours may be obtained.

Carey Lea's silver sols will be dealt with later (p. 687).

Colloidal lead, which is of interest in the treatment of cancer, has been prepared. Colloidal platinum may be obtained by the following method. 500 C.c. of chloroplatinic acid (0·1 per cent. solution) are made slightly alkaline with potassium carbonate. The solution is boiled, and then the flame is removed, and 2 to 4 c.c. of 33 per cent. acrolein added. A yellow sol is first formed, which gradually changes to black.

(b) *Oxidation.*—Colloidal sulphur may be prepared by the oxidation of hydrogen sulphide. If hydrogen sulphide is passed into a solution of sulphur dioxide in water until nearly all the odour of sulphur dioxide has been removed, the solution is found to contain sulphur, which will pass through a filter paper. The best way of dealing with this is to precipitate it all by boiling with sodium chloride, and then filtering. The precipitate is washed on the filter paper with distilled water until all sodium chloride has been removed. At the end of this process the sulphur begins to run through the paper, forming a fairly stable colloidal solution.

A good way of preparing a stable sulphur sol is to make solutions of well-washed hydrogen sulphide and sulphur dioxide. The strength of each solution is determined volumetrically, and the stoichiometrical amount of sulphur dioxide is added to a given volume of hydrogen sulphide solution.

Acidified sodium thiosulphate forms colloidal sulphur, but the sol is not very stable owing to the presence of electrolytes.

(c) *Exchange of Solvent.*—It is a general rule that if a substance A is soluble in B, but is insoluble in C, A will be thrown into suspension, usually colloidal, when a solution of A in B is added to an excess of C, the two solvents being miscible.

A sulphur sol can be made by adding a saturated solution of sulphur in alcohol to water. Phosphorus may also be obtained in colloidal solution in the same way. A good method of preparing a gamboge sol is by dissolving the substance in alcohol and then mixing with an excess of water.

A similar method is to decompose a complex salt, such as the complex potassium silver iodide obtained by dissolving silver iodide in an excess of potassium iodide, by adding much water to it. The silver iodide is then obtained as a sol.

(d) *Hydrolysis.*—This is the usual method for preparing oxide and hydroxide sols.

To prepare a sol of ferric hydroxide (or more accurately hydrated ferric oxide, the amount of hydration being uncertain), the addition of a few cubic centimetres of concentrated ferric chloride solution to much water (boiling) may be used.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl.$$

To ensure stability it is advisable to dialyse the product, but if all the hydrochloric acid is removed it becomes unstable, owing to the peptising action of the acid.

Zsigmondy prepared colloidal stannic acid by a similar method. A solution of stannic chloride is diluted so much that hydrolysis occurs. Wash by decantation, and peptise by means of ammonia.

Biltz prepared vanadic acid sols by the action of hydrochloric acid on ammonium vanadate. Five grams of ammonium vanadate are ground with a few drops of strong hydrochloric acid in a mortar. The product is suspended in water and filtered. The precipitate is washed well until it will pass through a filter paper, giving a red sol.

(*e*) *Double Decomposition.*—In many reactions where a precipitate might be expected, a colloidal solution results, and if special care is taken this may always be made the result. The application of von Weimarn's rules dealing with supersaturation gives us the correct conditions for this behaviour (§ 329).

Colloidal arsenic sulphide is readily prepared by making a 1 per cent. solution of arsenious oxide in hot water. The solution is cooled and filtered. To 200 c.c. of water saturated with hydrogen sulphide the solution of arsenious acid is added gradually, whilst a stream of hydrogen sulphide is passed through the solution. This is continued until an intense yellow sol is formed. The excess of hydrogen sulphide is removed by boiling or, better, by passing a stream of hydrogen through the solution.

Similarly, antimony trisulphide sols may be prepared. A 0·5 per cent. solution of tartar emetic is dropped from a tap funnel into water saturated with hydrogen sulphide and through which hydrogen sulphide is passed. A beautiful orange coloured sol of good permanency may thus be made.

An unusual colloid is manganese dioxide. Potassium permanganate, although a powerful oxidising agent, is slow in reacting with many substances. It will slowly react with ammonia to give nitrogen and manganese dioxide, the latter being formed in the colloidal state. Cuy recommends the following procedure: Heat a $M/100$ solution of potassium permanganate to boiling, and while stirring add strong ammonia solution, one drop every three minutes. There should never be a great excess of ammonia. Keep the solution at about 90° C. It turns wine red, and finally coffee brown by

transmitted light, and a bluish-brown oily colour by reflected light. To test if all the permanganate has been reduced, some of the colloidal solution may be coagulated by means of common salt. If there is any violet colour there is still some unchanged permanganate. The formation of colloidal manganese dioxide is apt to be a nuisance in the Volhard method of determining manganese volumetrically. Silica sol is easily prepared by the addition of acid to sodium silicate solution (water-glass). Commercial water-glass is diluted to a density of 1·16. 75 C.c. of the mixture are taken and 25 c.c. conc. hydrochloric acid and 150 c.c. water added, and the whole is dialysed. If the dialysis is carried too far the gel, in which colloidal silica usually exists, may form.

Silica gel can be made by mixing hot (50° C.), with constant stirring, a solution of hydrochloric acid containing 10 per cent. by weight of the gas, with an equal volume of sodium silicate solution

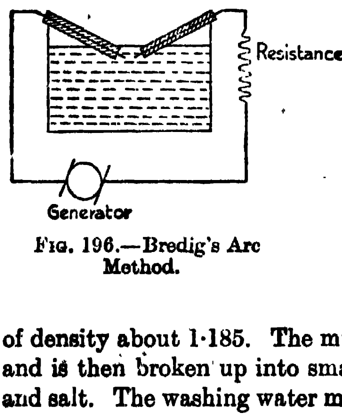


FIG. 196.—Bredig's Arc Method.

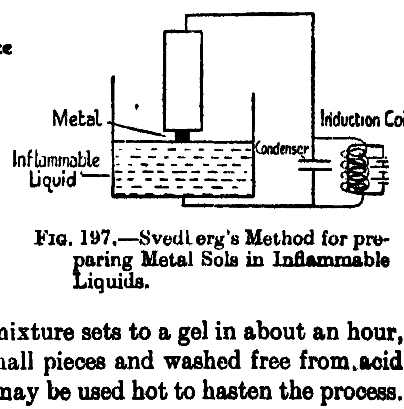


FIG. 197.—Svedberg's Method for preparing Metal Sols in Inflammable Liquids.

of density about 1·185. The mixture sets to a gel in about an hour, and is then broken up into small pieces and washed free from acid and salt. The washing water may be used hot to hasten the process. In drying, the water must be removed slowly. This is accomplished by passing a stream of air over the gel at 75° C. and increasing the temperature to 120° C., after which the temperature is slowly raised to 300° C. The final product is hard and transparent, something like glass in appearance. It is largely used, when activated by heating in air at a moderate temperature for a few hours, as an adsorbent of gases, and a dehydrating agent. It is used for drying the blast in iron smelting; it is the only cheap drying agent which can be used, and dehydrated on baking, an unlimited number of times (calcium chloride loses hydrogen chloride on heating after absorption of water). It may also be used for adsorbing colouring matters and other substances from solution, in a similar way to animal charcoal.

II. *Dispersion Methods.*—(*a*) *Bredig's Arc Method.*—This process consists in striking an arc beneath conductivity water between two

wires made of the metal to be dispersed. In preparing gold and some other sols, however, it is found advantageous to have in the solution a trace of sodium hydroxide or potassium carbonate. The vessel in which the dispersion takes place may be cooled in ice.

Svedberg prepared metal sols of sodium, etc., in inflammable liquids, using an oscillatory discharge, produced by passing the discharge from an induction coil provided with a condenser, through the metal in contact with the liquid. Svedberg states that in the formation of sols by the electro-dispersion method the metal is first vaporised, and the sudden cooling of the vapour gives rise to the colloid. It is usually found that the sols are contaminated with some oxide if formed in water.

(*b*) *Mechanical Dispersion.*—Comparatively recently "colloid mills" have been devised for grinding solids into particles of colloidal size. Actually they fail to do this completely, only a few of the particles formed being of colloidal diameter. The principle of the colloid mill is, in general, that the substance to be dispersed is suspended as a coarse precipitate in the dispersion medium and the liquid is then passed through a channel in which are two plates close together, rotating at high speeds (about 7,000 revolutions per minute) in opposite directions.

(*c*) *Peptisation.* This has already been mentioned (§ 332). Glue, gum, gelatin, etc., are soluble in water and give colloidal solutions, but actually they are peptised by the water.

A Prussian blue sol may be prepared by the process of peptisation. A 3 per cent. solution of potassium ferrocyanide is poured slowly into a 3 per cent. solution of ferric chloride. After a few minutes the precipitate is filtered off and washed well. A 5 per cent. solution of oxalic acid is then poured through the filter until the precipitate is peptised. Then the sol is dialysed to remove oxalic acid. The sol is quite stable.

334. The Molecular Weights of Colloids.—The osmotic pressures of colloids are very small, but have been measured, and give very high figures for the molecular weight. The difficulty in this type of determination is not only that the effect is small, but that the presence of small amounts of electrolytic impurities would have a comparatively great effect on the osmotic pressure. The presence of 0·05 per cent. sodium chloride would halve the apparent molecular weight of hæmoglobin, which is about 66,000. This objection applies to osmotic pressure methods, direct and indirect, but not to others, such as sedimentation and diffusion. Various other methods, such as depression of the freezing point, determination of coefficient of diffusion, and sedimentation, have been used for the determination of molecular weights of colloids, and in every case a high value is

obtained. The results of some experiments on this question are given in Table CIX.

TABLE CIX.—MOLECULAR WEIGHTS OF COLLOIDS

Substance.	Method Employed.	Molecular Weight.
Gelatin	Osmotic pressure	40,000
Glue	,, ,,	4,900
Gum arabic	,, ,,	3,000
Albumen	,, ,,	14,000
Horse serum albumen	,, ,,	72,000
Tungstic acid	,, ,,	1,700
Starch	Depression of the freezing point	25,000
Albumen	,, ,, ,, ,,	14,000
Ferric hydroxide	,, ,, ,, ,,	6,000
Silicic acid	,, ,, ,, ,,	5,000
Tannin	,, ,, ,, ,,	1,100
Invertase	Coefficient of diffusion	54,000
Emulsin	,, ,,	45,000
Albumen	,, ,,	17,000
Pepsin	,, ,,	13,000
Hæmoglobin	Sedimentation	66,800
Egg albumen	,,	34,500
Serum-globulin	,,	103,800
Hæmocyanin	,,	4,930,000

The coefficient of diffusion method has been studied and applied by Herzog. The diffusion coefficient D can be shown to be given by the equation

$$D = \frac{RT}{N} \cdot \frac{1}{6r\pi\eta} \qquad (1)$$

where N is Avogadro's number, r the radius of the particle, and η the coefficient of viscosity of the medium (p. 679). If it is assumed that the particles are spherical, then the molecular volume Mv is given by

$$Mv = \frac{4}{3}\pi r^3 N \qquad (2)$$

where v is the volume of 1 gm. (*i.e.*, the reciprocal of the density), and M is the molecular weight. Substituting the value of r obtained from this equation, in equation (1) we have

$$M = \frac{1}{162\pi^2 N^2} \cdot \left(\frac{RT}{\eta D}\right)^3 \cdot \frac{1}{v}.$$

This avoids the determination of r, and was the form of the equation used.

More recently the method of sedimentation has been employed by Svedberg.

This method is really based upon the fact that the size of a particle can be determined by the rate with which it falls through a medium (gaseous or liquid). This rate is called the velocity of sedimentation. An equation connecting the velocity of sedimentation with the particle size and the viscosity of the medium was first given by Stokes (see also the determination of the charge of the electron by Millikan, in which the size of oil drops was determined by applying a modified form of Stokes' equation, p. 70). This equation may be expressed in the form

$$r = \sqrt{\frac{9}{2} \cdot \frac{\eta v}{(\rho_p - \rho_d)g}}.$$

where r is the radius of the particle, η the viscosity of the liquid, v the velocity of sedimentation, ρ_p the density of the particle, ρ_d the density of the liquid, and g the acceleration due to gravity. The equation holds only for spherical particles falling freely (not near a wall).

The force of gravity is not sufficiently great to enable the size of very small particles to be determined by sedimentation. The force producing sedimentation can, however, be artificially increased by using a centrifuge. In the case of a particle falling freely through a medium under the action of gravity, two opposing forces act on the particle, the force of gravity and the frictional force which depends upon the viscosity of the medium through which the particle falls. In the case of the centrifugal force, this takes the place of the force of gravity, and the equation obtained is

$$\sqrt{\frac{9}{2} \cdot \frac{\eta \log_e \frac{x_2}{x_1}}{(\rho_p - \rho_d)\omega^2 t}}$$

In this equation x_1 and x_2 define the positions of a particle before and after falling; thus $x_1 - x_2$ is the distance through which the particle falls; ω is the angular velocity of the centrifuge, and t is the time occupied in falling. The other symbols have the same significance as before.

We are not so much concerned with determining the actual siz of the particles, as in determining their molecular weights. F this, Svedberg derives the equation

$$M = \frac{RT \log_e (x_2/x_1)}{D(1 - V\rho_d)\omega^2 t}$$

where D is the diffusion coefficient, V the partial specific volume (the solvent, and M the molecular weight of the particle.

In using this equation, D has to be determined separately; bu it is better to use the sedimentation equilibrium than the sedimenta tion velocity, as has just been done. After a time, an equilibriu will be reached, which in ordinary cases, where gravity only is th acting field, is governed by the equations mentioned in § 338.

Where the field is not due to gravity, but to the centrifugal forc

$$M = \frac{2RT \log_e (c_1/c_2)}{N(\rho_p - \rho_d)\omega^2(x_1^2 - x_2^2)}.$$

In this equation c_1 and c_2 are the concentrations of particles a points situated x_1 and x_2 cms. from the centre of rotation, and th other symbols have their former significance.

All that is necessary, then, to determine the molecular weight (the colloidal particle is to determine the relationship between th concentration of particles at two levels for a given speed of th centrifuge, the temperature being constant and known.

This equation has been used with considerable success by Svedber who devised an ultra-centrifuge for the purpose.[1] It could rotat at speeds up to 44,000 r.p.m., and could provide a field of forc 8,000 to 110,000 times the force of gravity. The axis of rotatio was horizontal. During the centrifuging, photographs of the cel containing the colloidal solution were taken at definite interva on the same plate and with the same exposure. If a sedimentatio equilibrium was to be studied, only those photographs taken whe equilibrium had been reached would be of use, but the others woul indicate whether equilibrium had been attained. After the centr fuging the cell was filled with the colloidal solution of differe concentrations, and these were photographed on the same plate a before, with the machine running, in order to provide standards fo judging the concentrations at various levels in the actual exper ment. After the plate was developed, the intensity of blackenin was investigated by means of a spectrophotometer, and from thes observations a curve could be drawn connecting concentration (the particles with the distance from the centre of rotation.

[1] A full description of the instrument cannot be given here; the student recommended to see Svedberg, "Colloid Chemistry," *Chemical Catal Co.*, 1928, pp. 146–180.

There is no doubt that this method of determining the molecular weights of colloids is more free from objections than others. The method can be applied to finding the size of any small particles, and for this reason in the early part of this discussion (p. 672) the theory was not confined to colloidal particles alone.

The Svedberg sedimentation method has given very valuable information concerning the molecular weights of proteins. All stable native proteins may be grouped into two classes according to their molecular weights: (1) Those with very high molecular weights, of the order of a million, such as hæmocyanin; the hæmocyanin of snail's blood (*Helix pomatia*) has a molecular weight of nearly five million; (2) those with a molecular weight of 34,500 to 207,000. These can be further subdivided into four groups, the molecular weights of the substances in each group being 1, 2, 3 and 6 times 34,500 respectively. Thus, egg-albumen has a molecular weight of about 34,500; hæmoglobin, about 68,000; serum-globulin, about 103,800; phycocyan and phycoerythrin, from algæ, about 208,000. The molecules of the first and last sub-groups are known to be spherical, and have a radius of 2·2 and 4·0 $m\mu$ respectively. The molecules of the other sub-groups are not spherical. The p_H of the solution is a deciding factor in the molecular weight of proteins. The hæmocyanin of the snail is only stable between p_H values of 7·3 and 4·3; outside this region, the molecular weight falls from 4,930,000 to 100,000. When the more complex protein molecules are degraded by chemical action, they give molecules of molecular weight 34,500 or some small multiple of this value. It would appear, then, that the molecular weight, 34,500, is a fundamental figure for proteins, and it has been suggested by Astbury that this "unit" molecular weight is that of a single protein chain, and that the 2, 3 and 6 multiples of this weight found in the four sub-groups just mentioned are crystallographic combinations due to the existence of 2-fold and 3-fold axes of symmetry. The value 34,500 is the approximate molecular weight of a single peptide chain.

The proteins mentioned above give definite, reproducible values for the molecular weight. They are called "monodisperse" systems; apparently all the particles have the same molecular weight. There are, however, some proteins, such as gelatin and casein, of which the particles vary in size. The molecular weight of gelatin varies from 10,000 to 70,000. Such systems are said to be "polydisperse."

335. The Investigation of Colloidal Solutions by Means of the Ultra-microscope.—It will never be possible to see atoms or molecules, or even colloidal particles, by means of the best microscope.

since it is impossible to get clear image-formation of objects smaller than the wavelength of the light employed. Tyndall, however, found that small particles were able to scatter light, and that the zone of scattered light was much larger than the particle itself, and could be seen in the microscope, or sometimes even by the naked eye. The same effect is noticed when a sunbeam enters a room. The atmosphere does not ordinarily appear to be dusty, but when the beam shines through, the dust particles are shown up. A colloidal solution when illuminated by a narrow beam of light appears opalescent when viewed at right angles to the beam. This opalescence is not found with pure water,[1] and is due to the scattering of the light by the very small colloidal particles. Under the microscope the actual zones of scattered light can be seen.

This principle was used by Siedentopf and Zsigmondy in 1903 for the construction of an instrument called the "ultra-microscope." The arrangement of the instrument is shown in diagrammatic form in Fig. 198. A strong beam of light from an arc lamp, or other powerful source L, passes through a slit S, and is condensed by a system of lenses so as to come to a focus in a cell containing the colloidal solution. This cell is placed on a microscope stage and viewed through the microscope in the ordinary way. Of course, the actual contours of the particles cannot be seen; they just appear as bright spots against a dark background. But at least the number of particles can be counted, and more recently it has been possible to decide the shape of the particles roughly. Suppose that in an experiment n particles were found in a field of view of volume v c.c., then, if the sol contains b grams per cubic centimetre (determined by evaporation and weighing) of the dry substance, of density d, the mean radius r of the particles will be given by

$$\sqrt[3]{\frac{3bv}{4\pi nd}}$$

This assumes two things. First, that the particles are spherical,

[1] It has been stated by Schade and Lohfert (1930) that the purest water, when sufficiently strongly illuminated, and viewed in the manner indicated above, does show a Tyndall beam. Especially is this so when ultra-violet light is used. The phenomenon cannot be explained as due to impurities, and the suggestion is made that it is produced by the existence of a certain small fraction of the water in a highly associated condition. It should also be noted that all transparent solids, liquids and gases scatter light, even when perfectly free from suspended dust, etc. The scattering agents are the molecules themselves (see Raman spectra, § 377). The phenomenon is, however, quite different from the Tyndall beam, in which a few localised scattering agents are visible as discrete bright spots. It is necessary to bear in mind this difference between the scattering of light by colloidal and other fine particles and by molecules.

and, secondly, that the density of a substance in the colloidal condition is the same as that in bulk, and there is no proof that this is so.

The limit of visibility in the ultra-microscope depends upon the optical nature of the colloidal particles and of the dispersion medium. It is found that colloidal metals give the best results, and can be detected down to a diameter of 6×10^{-7} cm. Organic particles can only be seen down to 4×10^{-6} cm.

Particles which are invisible even to the ultra-microscope are called amicrons.

In 1915, Freundlich and Diesselhorst found that it was possible to distinguish between spherical and non-spherical (or rod-like) particles in the ultra-microscope. Vanadium pentoxide and benzopurpurin form rod-like particles, which give a peculiar streaky appearance when they are stirred, and become doubly refracting

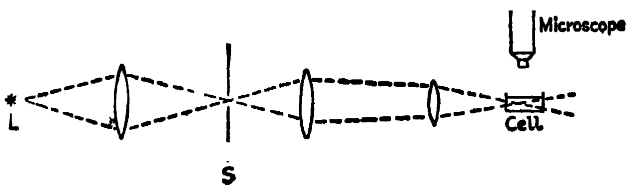


FIG. 198.—Arrangement of Ultra-microscope.

when flowing through a tube. The anisotropy is due to the rods all moving in one direction, with their axes in line, like a raft of logs floating down a river. This should be compared with the behaviour of liquid crystals (p. 279).

By examining various sols, Freundlich and Diesselhorst showed that those of gold (red), silver, platinum, arsenic sulphide and gamboge were spherical. The particles of aged ferric oxide and blue gold sols were disc shaped, whereas vanadium pentoxide, tungstic acid, and many colloidal dyestuffs gave rod-like particles.

Many colloidal particles have been shown by direct experiment with *X*-rays to be crystalline in nature, but, according to Kohlschutter's work, a large number of substances tend to have particles of definite form and shape, and yet are not crystalline. These are called "somatoids."

336. The Colours of Colloidal Solutions.—The colour of a sol will depend on its particle size, for upon this depends the nature of the light scattered by the particles. Like the colour of the sunset, the colour of colloidal solutions is due to light scattering. It should be possible, therefore, to calculate the size of particle required to give a certain colour, assuming that the particle is spherical in form.

This has been done by Mie, and his results have been verified experimentally by Schaum with silver sols, and by Feick with mercury sols. There is satisfactory agreement between the calculated and observed results, but this is not always the case.

The colour in many other cases is decided also by the shape of the particles, and at present no calculation has been made which takes this into account. Frequently, the specific absorption of light by the colloidal particles is of greater importance than the scattering in determining the colour.

337. The Brownian Movement.—In 1827 the botanist Robert Brown discovered that grains of pollen placed in water moved about ceaselessly. The cause of this motion was not suspected for many years, being at first ascribed to convection currents in the liquid. When colloidal solutions were examined under the ultra-microscope

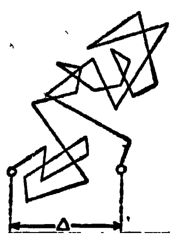


FIG. 199.—The Brownian Movement.

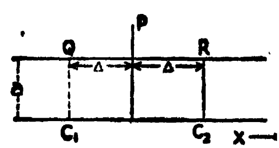


FIG. 200.

it was found that the particles in these solutions too were in constant motion, traversing no definite set path, but going in zig-zag directions all over the field of view. It was shown as the result of work by Wiener (1863), Ramsay, Delsaulx and Carbonelle, Gouy (1888) and others that the motion was independent (or nearly so) of the nature of the colloidal particle, but was more rapid the smaller was the particle, and the less viscous the solution. Wiener was the first to state that the movement was due to molecular motion. The small colloidal particles are knocked about by collision with the molecules of the dispersion medium.

At first sight it would appear difficult to make any accurate observations on the motion, which is so haphazard. However, it is possible to calculate what the probable displacement of a particle will be after a given time. This displacement may be conveniently measured as a projection on any axis we may choose to take, x (see Fig. 199).

Take now a cylinder of the sol of area of cross-section a (Fig. 200). Consider a plane P in it, and let the concentration of sol be c_1 at a

distance Δ to the left of P (*i.e.*, at the plane Q) and c_2 at a similar distance to the right of P (*i.e.*, at the plane R). We shall consider only the components of the particles parallel to the x-axis, as we wish to calculate the number of particles which will cross from one side of the plane P to the other in the small time t. Let the mean value of the displacements parallel to the x-axis in the time t be Δ. The particles arriving at P from the left are only those whose distance from the plane P is less than Δ. Moreover, only half of these may be taken as moving towards the plane, since by probability half of them will be moving in the opposite direction. Similarly for those moving from the right across P. The number of particles crossing P in time t is therefore

$\frac{1}{2}a\Delta$ (mean concentration in region PQ — mean concentration in region PR),

$$= \tfrac{1}{2}a\Delta\frac{(c_1 - c_2)}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value of the concentration gradient, $\frac{dc}{dx}$, is given by

$$\frac{-dc}{dx} = \frac{(c_1 - c_2)}{2\Delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence, substituting for $(c_1 - c_2)$ in (1), the number of particles crossing P in one second is

$$-\tfrac{1}{2}\frac{a}{t}\Delta^2\frac{dc}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now, the *diffusion coefficient D* is *defined* as the number of particles passing in unit time across a plane of area 1 sq. cm., the concentration gradient being unity. Hence, putting $a = 1$, and $\frac{dc}{dx} = 1$, we have

$$D = \tfrac{1}{2}\frac{\Delta^2}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence, the square of the mean displacement of the particles, Δ^2, is proportional to the time t, during which the displacement occurs.

It is possible from this to deduce a relationship between the coefficient of diffusion, the size of the particles, and the viscosity of the liquid. The derivation is due to Einstein. If the velocity of the moving particle is u, k is the force causing its motion, and F the frictional resistance,

a solution is considered of concentration c gm.-mols. per unit vol., we have for the diffusion across a given plane

$$u = \frac{1}{cN} \cdot \frac{K}{F} \quad \ldots \ldots \quad (5)$$

where K is the total force acting on all the particles, and N is Avogadro's number (cN will be the number of particles in unit volume, since N is the number of molecules in 1 gm.-molecule). The force acting on the particles is the gradient of osmotic pressure, P.

$$\therefore \quad K = -\frac{dP}{dx}.$$

The relationship between the pressure P and the concentration c is approximately

$$P = RTc.$$

Hence, $$K = -RT\frac{dc}{dx} \quad \ldots \ldots \quad (6)$$

Substituting for K in (5), we get

$$uc = -\frac{RT}{NF} \cdot \frac{dc}{dx}. \quad \ldots \ldots \quad (7)$$

The relationship between the frictional resistance F to the motion of a particle of radius r, in a liquid of viscosity η, is

$$F = 6\pi\eta r \quad \ldots \ldots \quad (8)$$

Substituting this value of F in (7), we have

$$uc = -\frac{RT}{6\pi\eta r N}\frac{dc}{dx} \quad \ldots \ldots \quad (9)$$

uc is the amount of substance passing through unit section in unit time; when $-\frac{dc}{dx}$ is equal to unity, this quantity uc is the diffusion coefficient D. Hence

$$D = \frac{RT}{6\pi\eta N r} \quad \ldots \ldots \quad (10)$$

We can now substitute this value of D in (4), obtaining

$$\Delta^2 = \frac{RTt}{3N\pi r\eta} \quad \ldots \ldots \quad (11)$$

Now, all the quantities can be measured in this equation except N and hence the method can be used for determining Avogadro's number.

This equation has been tested by Perrin and others, whose results are given in Table CX.

TABLE CX.—VALUES OF AVOGADRO'S NUMBER FROM EXPERIMENTS BASED ON THE BROWNIAN MOVEMENT

Nature of Colloidal Solution.	Radius of Particles in μ.	$N \times 10^{-23}$.
Gamboge in water	0·367	6·9
Gamboge in 35 per cent. sugar solution	0·212	5·5
Mastic in water	0·52	7·3
Mastic in 27 per cent. urea solution .	5·50	7·8
Gamboge in 10 per cent. glycerin solution	0·385	6·4

338. The Distribution of Colloidal Particles under Gravity.—After standing for some time a colloidal solution will be found to deposit the colloid. It is clear that by the very action of gravity alone the greater number of particles will be found at the bottom of the vessel, and that their vertical distribution will be exponential. Assuming that the particles obey the gas laws, the distribution of particles will be the same as the distribution of the atmosphere, the density of which is greatest near the earth's surface. It can be shown quite easily that if D_1 and D_2 are the densities of particles (*i.e.*, number of particles in a given volume) at heights h_1 and h_2 respectively, and if M is their molecular weight, and T the absolute temperature

$$\log_e \frac{D_1}{D_2} = \frac{Mg(h_2 - h_1)}{RT}.$$

Instead of the molecular weight M, we may write for a colloidal solution mN, where m is the mass of one particle (or the mean mass of the particles) and N is Avogadro's number. For m we may put VD, where V is the volume of a particle and D is the effective density of the colloid in the solution which (on account of the upthrust) is equal to its absolute density D_e minus the absolute density of the dispersion medium, D_m. Hence,

$$\log_e \frac{D_1}{D_2} = \log_e \frac{n_1}{n_2} = \frac{NV(D_e - D_m)g(h_2 - h_1)}{RT}.$$

n_1 and n_2 being the average number of particles in any given volume at the two heights.

Perrin also used this equation to calculate N. He determined n_1 and n_2 by direct counting, having taken a photograph of the particles at the two levels chosen. The distance between the levels was determined by the focussing screw on the microscope, the readings being taken when the two levels were focussed. Perrin prepared particles of gamboge and of mastic of any desired size by a centrifugal machine. He measured their volumes and diameters by several methods which all gave results agreeing with each other. Knowing the volume of the particles he could calculate N. This he found to be 6×10^{23}, which agrees closely with the value obtained by quite different methods, and thus indicates the accuracy of the arguments about the motion of colloidal particles (see Chapter V., § 79).

339. Electrical Properties of Colloids.—If the lower part of a U-tube of the form shown in Fig. 201 is filled with ferric hydroxide sol, and then distilled water is poured over this, it is found that when a high potential is applied between electrodes placed in the water, the boundary between the colloid and the distilled water begins to move. This movement must indicate that the colloidal particles themselves are electrically charged, and behave somewhat as ions do under similar circumstances (see Lodge's experiment, p. 527). This motion of colloid particles under the action of an electric field is called *cataphoresis*. It has been suggested that since this term seems to indicate motion towards the cathode, which is not by any means always the case, a better term would be *electrophoresis*.

If this experiment is tried with various colloids, it is found that some move towards the anode and some towards the cathode. Hence some colloids bear a positive and others a negative charge. The majority of sols are charged negatively. The metals and the sulphides are the chief members of this class. The metallic hydroxides and oxides, and basic dyestuffs, are positively charged. The Table below shows the two classes.

TABLE CXI.—CHARGES ON COLLOIDS DISPERSED IN WATER

Positively Charged.	Negatively Charged.
The hydroxides, *e.g.*, $Fe(OH)_3$, $Cd(OH)_2$, $Cr(OH)_3$, $Al(OH)_3$, etc.	The sulphides, *e.g.*, As_2S_3, Sb_2S_3, CdS, etc.
The oxides, *e.g.*, TiO_2, etc.	The metals, *e.g.*, Ag, Au, Pt.
Basic dyes.	Organic colloids, *e.g.*, gum arabic, starch, gamboge.
	Acid dyes.

The absolute mobility of the particles can be determined just as the absolute velocity of ions is found by the moving boundary method. The result obtained for colloidal gold or silver is in the neighbourhood of $2 - 3 \times 10^{-4}$ cm. per sec. for a potential gradient of 1 volt per cm. This is about the absolute velocity of organic ions of high molecular weight, and it has been suggested by Hevesy that there is not a great difference in these two classes, because for a colloidal particle the mass and the charge have increased in approximately the same proportions. The chief difference will be caused by viscosity.

In what way is this charge obtained? In the case of the electrolytic colloids, such as sodium palmitate and the soaps in general, the answer is that ions are produced, and the charge is definitely ionic. But this explanation will not hold for non-electrolytes. It was thought at first that the charge was caused by friction, but this has not proved to be the correct explanation. The probability is that the colloidal particles adsorb ions present in the dispersion medium. This view was put forward by Hardy, who showed that it was possible to change the sign of the charge on a colloid by placing it in an environment of ions of an opposite sign to that which it had. Thus mastic when suspended in water is found to have very little charge indeed, but when placed in an acid solution it becomes charged positively, presumably because of adsorption of hydrogen ions; and in alkaline solution it becomes charged negatively, owing to adsorption of the negatively charged hydroxyl ions.[1] This would also explain the fact that the solution as a whole is always electrically neutral. If the charge were frictional, the whole liquid should bear a charge.

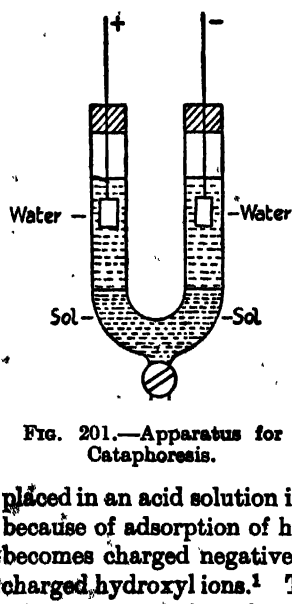


FIG. 201.—Apparatus for Cataphoresis.

This is also shown by mobility experiments with silver sols in the presence of aluminium sulphate (Svedberg, 1907, and others). The mobility decreases as the negatively charged silver ion adsorbs more

[1] The same effect is noted with egg albumen, but the explanation is probably different. All proteins are complex amino-acids of the type $NH_2 - [X] - COOH$. They form ions $^{+}NH_3 - [X] - COOH$, $\overset{+}{N}H_3 - [X] - COO^-$, or $NH_2 - [X] - COO^-$. The first is formed in acid solution, the last in alkaline solution. The second or Zwitter-ion (§ 298) is present at the isoelectric point. The lyophilic colloids do not precipitate at this point, but their solubility is a minimum there.

of the positively charged Al^{+++}, until it can actually be reversed. At a certain point the silver particles will bear no charge.

TABLE CXII.—VARIATION OF MOBILITY OF SILVER SOL WITH ADDITION OF Al^{+++}

Gms. of Al^{+++} added per 100 c.c. of Ag Sol.	Mean Mobility. cm./sec/volt.
0	$2 \cdot 0 \times 10^{-4}$
$1 \cdot 7 \times 10^{-5}$	$1 \cdot 28 \times 10^{-4}$
$3 \cdot 5 \times 10^{-5}$	$1 \cdot 03 \times 10^{-4}$
$5 \cdot 2 \times 10^{-5}$	$0 \cdot 26 \times 10^{-4}$
$6 \cdot 1 \times 10^{-5}$	0
	(Direction reversed)
$6 \cdot 9 \times 10^{-5}$	$- 0 \cdot 42 \times 10^{-4}$
$8 \cdot 7 \times 10^{-5}$	$- 0 \cdot 61 \times 10^{-4}$
$17 \cdot 3 \times 10^{-5}$	$- 1 \cdot 56 \times 10^{-4}$

This is called *the isoelectric point.* At this point the colloid coagulates. This process of coagulation is not as a rule itantaneous, and hence it is sometimes possible to change the n of the charge on the colloidal particle by passing through the electric point rapidly.

It is now seen why it is necessary not to dialyse colloids too much.

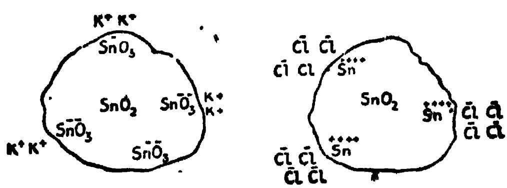


FIG. 202.—Positive and Negative Stannic Oxide Particles.
[After Fig. 13 of Dr. E. S. Hedges, *Chapters in Modern Inorganic and Theoretical Chemistry* (Edward Arnold & Co.).]

If all the ions were washed away, the particles would be left uncharged and would coagulate.

The origin of the charge on the particles is still a matter of some doubt. We know that ions are adsorbed, but where do they come from? It is thought that an electrical double layer is formed on the surface of the particle (Helmholtz). Take the case of stannic hydroxide. This sol is peptised by potassium hydroxide, and the particles then have a negative charge. It is not probable that the hydroxyl ions are adsorbed directly, but that the potassium

hydroxide reacts with the stannic oxide at the surface to produce potassium stannate, which dissociates forming potassium ions and stannate ions. These form the electrical double layer. In a similar way, stannic oxide can be peptised by hydrochloric acid ; a little stannic chloride is probably formed at the surface, which then ionises, giving a double layer composed of stannic and chloride ions. These are so oriented that the Cl^- ions turn out towards the water, and the stannic ions towards the stannic oxide particle, thus making it positively charged.

Since the particles of a colloidal solution are charged, and move under the influence of a field, it follows that if the particles are kept still the dispersion medium must move. This movement is called *electro-osmosis*. A suitable apparatus for demonstrating this is

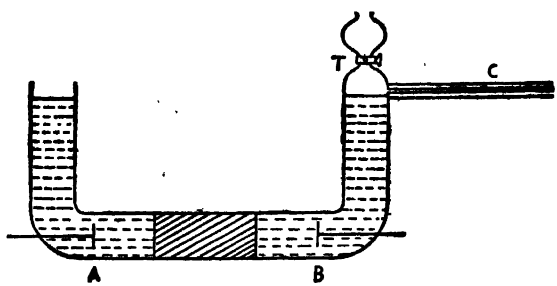


FIG. 203.—Apparatus for Electro-osmosis.

shown in Fig. 203. A U-tube has one limb closed with a tap, and is provided with a sealed-on capillary tube C.

The particles are made into a porous block shown in the centre of the tube. This block may consist, say, of porous earthenware, when the electro-osmosis due to the clay particles is measured. The vessel is filled with water until it just enters the capillary. On passing a current between the electrodes A and B, water will rise or fall in the limb T according to the direction of the current. This is then arranged so that the liquid rises in T. The rate at which the water moves along the capillary C, is a measure of the electro-osmosis.

340. Coagulation of Colloids by Electrolytes.—If an electrolyte is added to a sol, precipitation frequently occurs. This coagulation of colloids by electrolytes, to which reference was occasionally made in the description of the methods of preparation of colloids (§ 333), was investigated by Hardy and Schulze, Freundlich, Zsigmondy, and others.

If our view as to the nature of the charge on the particles is

correct, it follows that coagulation will be brought about by the agency of an ion bearing an opposite charge to that on the particle. This was found to be the case. In the precipitation of the positively charged ferric hydroxide sol, it is the anion which is of importance. It does not greatly matter what the cation is. It is known that adsorption of the ions of the added electrolyte occurs when coagulation takes place, since the coagulated colloid always drags down with it some of the precipitating substance. A certain minimum amount of electrolyte is necessary to bring about coagulation, and this amount varies with the valency of the added ions. The following Table gives the minimum amounts of various electrolytes required to coagulate a given amount of arsenious sulphide sol. The amount is expressed in millimols of electrolyte required per litre of sol.

TABLE CXIII.—COAGULATION OF As_2S_3 SOL (1·85 gms./litre)

Univalent Cations.	Coag. Value.	Bivalent Cations.	Coag. Value.	Tervalent Cations.	Coag. Value.
LiCl	58	$MgSO_4$	0·81	$AleCl_3$	0·093
NaCl	51	$MgCl_2$	0·72	$Al(NO_3)_3$	0·095
KCl	49·5	$CaCl_2$	0·65	$\frac{1}{2}Al_2(SO_4)_3$	0·096
KNO_3	50	$SrCl_2$	0·63	$Ce(NO_3)_3$	0·080
$\frac{1}{2}K_2SO_4$	65·5	$BaCl_2$	0·69		
		$ZnCl_2$	0·68	Mean	0·091
Mean	54·8	$(UO_2)(NO_3)_2$	0·64		
HCl	31	Mean	0·69		
$\frac{1}{2}H_2SO_4$	30				

The Law of Hardy and Schulze states that *the coagulating effect of an ion depends upon its valency*. It is clear that the Law is satisfied by the data in Table CXIII. The coagulating powers of univalent cations are all approximately the same, as are those of bivalent and tervalent cations. Yet between the classes there are great differences. Much more of a univalent cation is required than of a bivalent, and much more of a bivalent than of a tervalent ion. Taking a rough average of the figures quoted, it is seen that univalent cations have a coagulation figure of about 54·8 (omitting the figures for the acids, which are obviously out of place); that for bivalent cations is about 0·69, and for tervalent cations about 0·09.

If electrolytes can bring about coagulation, it is obvious that if two oppositely charged colloids are mixed, coagulation of both will occur, if the total amount of charge on each is equal. If not, partial coagulation only will occur.

The coagulation of a colloid by the addition of an electrolyte is by no means as simple as the above account would lead one to think. It has been found that the amount of electrolyte required to precipitate a given amount of a colloid seems to depend upon the rate at which it is added. There are many complicating factors.

341. Protection of Colloids.—If a stable organic colloid, such as gelatin, is added to a metal sol, the latter may be prevented from coagulating on the addition of an electrolyte. Also, the sol may now be evaporated to dryness, and on treatment with water will redissolve as a colloidal solution. Thus its behaviour is altered from that of an irreversible colloid to that of a reversible one.

Zsigmondy, in order to measure the relative protecting powers of organic colloids, originated the principle of the *gold number*. The gold number of a protective colloid is the quantity in milligrams of the added colloid which is able to protect 10 c.c. of a red gold sol (0·5 to 0·06 gm. of gold per litre) from coagulation by the rapid addition of 1 c.c. of a 10 per cent. solution of common salt. The gold sol must be specially prepared according to a given recipe. It is clear from the nature of this definition that the gold number is not a very accurate constant for a colloid. Some gold numbers are given in Table CXIV.

TABLE CXIV.—GOLD NUMBERS

Sol.	Gold Number.
Gelatin	0·005– 0·01
Casein	0·01 – 0·02
Hæmoglobin . . .	0·03 – 0·07
Albumen	0·1 – 0·2
Gum arabic . . .	0·15 – 0·25
Dextrin	6 – 20
Potato starch . . .	20 – 25
Colloidal SiO_2 . .	No protective action

Protective action is a very important phenomenon. It enables colloids to be kept when otherwise spontaneous change would take place. Thus, if potassium iodide is added to mercuric chloride solution, a red precipitate of mercuric iodide is formed. It is well known that the yellow form is produced first and that it immediately changes to the red form. If now potassium iodide is added to a solution of mercuric chloride to which some gelatin has been added, a yellow colloidal form of the iodide is produced which does not coagulate, and may be kept for years.

By this means it has been found possible to prepare colloidal solutions of the metals of high concentration. Carey Lea prepared silver sols containing 99 per cent. silver by reducing silver nitrate with mixtures of ferrous sulphate and sodium citrate. The organic matter which they contain acts as a protective colloid for the silver. Such sols are used in medicine for intravenous injection, or as an ointment.

Paal and Amberger have used sodium protalbate and sodium lysalbate (decomposition products of the proteins) for protection of metallic sols with very good results.

In the commercial preparation of ice cream, a little gelatin is added as a protective colloid, to give the cream a smooth taste. If it were not added, small gritty crystals of ice and lactose would separate.

342. Colloids and Analysis.—In qualitative analysis, colloidal solutions are frequently met with. In the precipitation of the sulphides in Group II by hydrogen sulphide, colloidal sulphur is frequently formed. We now see how this may be removed. The addition of an electrolyte will cause coagulation. It is not permissible to add any electrolyte at will, but ammonium chloride can be added. The addition of this substance also helps to ensure complete precipitation and easy filtration of the sulphides of Group IV. One is always told to remove organic matter before starting on a qualitative analysis. This is because the organic substance may form a protective colloid, and prevent the complete precipitation of the various group precipitates.

In the separation of zinc from manganese by "dissolving" the zinc hydroxide in sodium hydroxide, it is very probable that sodium zincate is not formed at all, but that the zinc hydroxide is peptised by the alkali, since on passing the solution through an ultra-filter zinc hydroxide is kept back.

This matter is of great importance in gravimetric analysis. One of the chief sources of error here is in the adsorption of substances by the precipitate, and it is often a very difficult matter to remove these adsorbed impurities. Adsorption will depend upon particle size (§ 343) being greater the smaller the particle, and this in turn is governed by von Weimarn's rules (§ 329). It is therefore clear that the temperature and concentration of the reactants are important considerations in gravimetric analysis. To prevent adsorption as much as possible, the precipitation should be carried out at the boiling point and fairly strong solutions should be used.

Colloids have great application in industry, particularly in adsorption. Large quantities of silica gel are manufactured for use in adsorption of gases, for which it is as effective as charcoal. It is

probable that dyeing is a colloidal process. The treatment of sewage is also a colloidal problem, since the impurities are largely present in the form of sols. Colloidal chemistry is also of importance in the study of the soil, in the manufacture of paints, in tanning. It also has a great deal to do with biological processes, but a full treatment of these would be outside the scope of this book.

343. Adsorption.—The Gibbs Adsorption Law.—When the concentration in the interfacial layers between two phases is greater than in the bulk of either phase, then the substance is said to be adsorbed at the interface.

Many solid substances have the power of adsorbing moisture. Particularly do glass and porcelain possess this property. Some porous substances have the power of adsorbing gases.

Adsorption is a surface phenomenon, and hence it will increase in importance as the particles are made smaller, for then a larger surface is presented by a given substance. Adsorption differs from absorption in being confined largely to the surface of the adsorbent. It is observed at the surface of a solution. It was shown theoretically by Gibbs that those *substances which lower the surface tension* (§ 99) *of a solvent in which they are dissolved become concentrated in the surface layer, whilst the concentration of substances which raise the surface tension is less in the surface layer than in the bulk of the solution.*

Thus when many inorganic salts are dissolved in water they increase the surface tension slightly, so that the concentration of the salt in the top layer of the solution will be less than in the bulk of the liquid. On the other hand, many organic substances, such as esters, aldehydes and ketones, lower the surface tension, and are therefore more concentrated in the top layer than in the bulk of the solution.

The mathematical expression, derived by Gibbs, governing this variation in concentration is

$$-S = \frac{C}{RT} \cdot \frac{d\gamma}{dC},$$

where S is the excess of solute in the surface layer; the sign indicates whether there is actually an excess or a deficit; C is the concentration of solute if equally distributed, R is the gas constant, T is the absolute temperature, and γ is the surface tension. $\frac{d\gamma}{dC}$ is, of course, the variation of surface tension with concentration, and can be obtained by plotting γ against C; $\frac{d\gamma}{dC}$ is the slope of this curve at the point at which the conditions are those of the experiment.

Direct experimental proof of this law is difficult with inorganic salts, and has not yet been carried out. However, semi-quantitative results have been obtained with certain organic liquids as solutes. Miss Benson (1903) studied a solution of amyl alcohol in water. Amyl alcohol lowers the surface tension of water considerably. On shaking the solution, a froth was obtained, and it was shown that the froth contained more amyl alcohol for a given volume than the bulk of the solution, as would be expected.

Actually the Gibbs Adsorption Law was first derived for the solution of gases in liquids. If a gas, on solution in a solvent, increases the surface tension, the concentration of gas in the top layer of the solution will be less than in the bulk of the solution, and if, on solution, the surface tension is decreased, the concentration will be greater in the surface layer. The equation here is

$$-S = \frac{p}{RT} \cdot \frac{d\gamma}{dp},$$

where p is the partial pressure of the gas, and the other terms have their previous significance. Again, this formula has not been proved quantitatively, though it is known qualitatively that such an adsorption takes place.

As the Gibbs equation shows, low temperatures will favour adsorption. There need not be chemical change when adsorption takes place, though frequently there appears to be some such change. It is a matter of great importance in connection with heterogeneous catalysis (§ 352).

Many solids adsorb gases. The removal of such adsorbed layers of gas is a problem which is of frequent occurrence. It has already been mentioned that glass and porcelain take up moisture. This layer must be removed before carrying out any quantitative experiments involving change of temperature, as otherwise the mass of the adsorbed moisture at the end of the experiment may be different from that at the start. The removal may be effected by heating the vessel to redness, and allowing it to cool in a desiccator. In the construction of discharge tubes for studying the conductivity of gases and the production of spectra, and in the manufacture of wireless valves, where a great deal depends upon the maintenance of a high vacuum, it is necessary to "outgas" the various metal parts and the glass of the tubes by heating to redness *in vacuo*. Otherwise, when the vacuum in the tube had been created, the gas would slowly be given up by the metal parts and the glass, causing an appreciable pressure.

The removal of adsorbed gases also plays an important part in paint manufacture. Unless the solid particles of colouring matter

are directly in contact with the linseed oil in which they are suspended, the paint will not adhere well to the surface to be painted, and will have a poor covering power. The gases are removed by continued grinding with the oil.

The process of adsorption of gases by solids, however, has its uses, as well as its disadvantages. Some porous substances, such as charcoal (particularly coco-nut charcoal) adsorb gases very readily. Reference to this has already been made (§ 197) in connection with the removal of the last traces of gas from an "exhausted" tube. The adsorption of gases by silica gel (p. 669) is a process of technical importance.

The adsorption of colouring matters from solution by animal charcoal is an example of the same phenomenon, and is a process of great technical importance in the refining of sugar. The brown sugar solution is warmed and allowed to stand in contact with animal charcoal for some hours. The colourless solution is then run off.

Adsorption is frequently a nuisance in gravimetric and qualitative analysis. Reference has already been made to the contamination of precipitates by adsorbed substances (§ 122), and the errors caused in results. Even thorough washing does not completely remove the impurities. In qualitative analysis, the hydroxides of zinc and calcium are frequently adsorbed by ferric hydroxide, so that if the first two metals are only present in traces in the original iron-containing mixture, they may not be detected, being completely adsorbed by the ferric hydroxide.

Ferric hydroxide is a good adsorbent for arsenic from sodium arsenite, and is used as an antidote for arsenic poisoning.

344. Distinction between Absorption and Adsorption.—The essential difference between absorption and adsorption lies in the fact that the latter is a surface phenomenon, and the former concerns the whole mass of the absorbent. In practice, it will be expected that in the case of adsorption, equilibrium will be attained rapidl[y] whereas in the case of absorption it will be reached more or le[ss] slowly.

The experimental distinction

carried out by McBain (1909). When charcoal takes up hydroge[n] at the temperature of liquid air, both absorption and adsorptio[n] appear to occur. Charcoal saturated with hydrogen was place[d] in a vessel which could be exhausted, and which was provided wit[h] a manometer. When the vessel was exhausted, the hydrogen w[as] removed from the charcoal in two stages. Some was remove[d] rapidly, the rest very slowly. The first amount removed was th[at] adsorbed on the surface, the second that absorbed by the interi[or]

of the charcoal. Similar phenomena were observed when the reverse change took place. An "outgassed" charcoal was placed in an atmosphere of hydrogen. Within two minutes 99 per cent. of the hydrogen that could be taken up by the charcoal was adsorbed. The remaining 1 per cent. was taken up slowly, corresponding to a slow diffusion into the interior of the charcoal.

McBain proposed the use of the term *sorption* to cover the whole phenomenon of the taking up of a gas by a solid. The surface effect is *adsorption*, the solution in the interior of the substance is *absorption*. These terms are universally accepted.

345. Determination of the Amount of Sorption.—This is usually done by first freeing the substance from gases already taken up by heating *in vacuo*. A weighed amount of the substance is taken. After evacuating, and cooling, a measured amount of gas is admitted, and the pressure and volume noted after waiting until no more gas is taken up. From these values the amount of gas taken up can be found.

346. The Adsorption Isotherm.—If x is the mass of gas adsorbed, and m the mass of the adsorbent, and p is the pressure of the gas,

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

where a and n are constants. This relationship was obtained empirically by Freundlich, and is known as the *adsorption isotherm*. It has no theoretical significance, and holds only for medium gas pressures.

In the case of adsorption from a solution, the equation becomes

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

where c is the equilibrium concentration of the adsorbed substance in the solution.

Taking logarithms, we have

$$\log x - \log m = \frac{1}{n} \log c + \log a,$$

so that if $\log x$ is plotted against $\log c$, a straight line should be obtained.

The adsorption isotherm bears a certain formal similarity to the Distribution Law (§ 216). If the concentration of a substance distributed between two immiscible liquids is c_1 in the first substance and c_2 in the second, and if n is the degree of association of the solute in the second solvent,

Hence
$$c_1 = \sqrt[n]{kc_2}$$
$$= k_1 c_2^{\frac{1}{n}}.$$

It will be seen that this is very similar to the adsorption isotherm. It cannot, however, be argued that the value of n indicates the extent of association in the adsorbed layer.

The following data for the adsorption of argon by coco-nut charcoal at $-$ 78·3° C. illustrate the law.

TABLE CXV.—ADSORPTION OF ARGON BY COCO-NUT CHARCOAL AT $-$ 78·3° C. (Miss Homfray, 1910).

: 3·698 ; $\frac{1}{n}$: 0·6024.

p (cm. of Mercury).	$\frac{x}{m}$ (Obs.).	$\frac{x}{m}$ (Calc.).
5·42	9·9	10·2
9·84	15·4	14·7
12·9	18·6	17·3
21·8	24·0	23·7
56·4	39·4	41·9

Adsorbed substances, especially gases, frequently show enhanced activity. Thus hydrogen adsorbed on palladium will act very much like nascent hydrogen. It will precipitate mercury from mercuric chloride, and reduce ferric chloride. This is of importance in connection with the theory of catalysis (§ 352).

347. Adsorption Indicators.—Within recent years various dye-stuffs, which owe their use to adsorption, have been introduced as indicators, particularly in silver titrations. Thus potassium bromide is conveniently titrated with silver nitrate, using eosin as an indicator. When the silver nitrate is run into the bromide a precipitate of silver bromide is produced, which, however, can adsorb either silver or bromide ions, the latter preferentially. It can also adsorb the dye eosin. When silver ions are adsorbed they are adsorbed as their eosin salts, which are brick-red. Thus so long as there is excess bromide present, the bromide ions will be adsorbed in preference to silver, and the solution retains the colour of the eosin, a pinkish-yellow. As soon, however, as there is a slight excess of silver ions, these are adsorbed on the silver bromide formed, together with eosin, and give the precipitate a brick-red colour. The indicator is extremely useful for dilute solutions, and will give

accurate results with concentrations down to $M/1,000$. Fluorescein is also used in the determination of chlorides by means of silver nitrate. It is important to remember that it is not the colour of the solution which changes, but that of the precipitate. Other dyes which will act as adsorption indicators in silver titrations, and some other precipitation titrations are, dichlorofluorescein, di-iodo-fluorescein, and other fluorescein derivatives, Biebrich scarlet, pheno-safranine, tartrazine, and rhodamine 6 G.

SUMMARY

A colloidal solution is a two-phase system consisting of a disperse phase (small particles, or drops) and a dispersion medium (gas, liquid, or solid). A large number of substances can exist in the colloidal state.

Colloidal solutions are referred to as sols. They may be classified as lyophobic and lyophilic sols. Lyophobic sols are not very stable, and once precipitated do not pass back into the colloidal state on adding the dispersion medium. They are therefore irreversible. This class includes the inorganic sols. Lyophilic sols are more stable and are reversible. This class comprises the organic sols and a few inorganic ones.

Another classification distinguishes between colloidal electrolytes, such as the soaps, and non-conducting colloids.

Colloids are unable to pass through certain membranes (*e.g.*, parchment), and can thus be separated from salts and other non-colloids, which will pass through. The process is called "dialysis."

Peptisation is the formation of a colloidal solution from a substance known to be capable of forming such a solution, by treating it with an electrolyte.

The methods of preparing colloidal solutions are :—

I. Condensation methods. (*a*) Reduction (*e.g.*, Au) ; (*b*) Oxidation (*e.g.*, S) ; (*c*) Exchange of solvent ; (*d*) Hydrolysis ; (*e*) Double decomposition.

II. Dispersion methods. (*a*) Bredig's arc method ; (*b*) Mechanical dispersion (colloid mills).

The molecular weights of colloids are very high. They may be found by the usual methods for solutes (colligative properties) and by diffusion and sedimentation. The last is the best method.

Colloidal solutions give the Tyndall beam when a strong beam of light is passed through them. This provides a method of observing colloidal particles (ultra-microscope) which has been widely used. Such particles are found to be in motion, executing a zig-zag course (Brownian Movement). By studying this, Einstein and Perrin have been able to deduce the Avogadro number, N, obtaining a value in agreement with that obtained by other methods.

The particles in a colloidal solution are electrically charged. They are attracted towards electrodes placed in the solution in a way similar to ions (electrophoresis). Some colloids are charged positively and others negatively. By the agency of ions charged oppositely to the colloidal particles, the latter are discharged and the colloid precipitates. The precipitating power of an ion depends on its valency (Hardy

Schulze Law). The addition of a lyophilic sol to a lyophobic one frequently protects the latter from coagulation by electrolytes.

When the concentration of a substance in the interfacial layers between two phases is greater than in the bulk of either phase, then the substance is said to be *adsorbed* at the interface.

Substances which lower the surface tension of a solvent in which they are dissolved become concentrated in the surface layer; substances which increase the surface tension are less concentrated in the surface than in the bulk of the solution (Gibbs' Adsorption Law).

The adsorption of substances also finds empirical quantitative expression in the Freundlich adsorption isotherm.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 42.—Prepare some colloidal solutions according to the instructions given on pp. 465–670.

Experiment 43.—Compare the effects of solutions of potassium chloride, calcium chloride, and aluminium chloride in coagulating an arsenic sulphide sol.

Make up some arsenic sulphide sol and place 10 c.c. of it in each of nine clean test-tubes. Add to the tubes the following mixtures:—

(*a*) 5 c.c. 0·1 M KCl + 5 c.c. water.
(*b*) 1 c.c. 2·0 M KCl + 9 c.c. water.
(*c*) 2 c.c. 2·0 M KCl + 8 c.c. water.
(*d*) 0·5 c.c. 0·1 M $CaCl_2$ + 9·5 c.c. water.
(*e*) 2·0 c.c. 0·1 M $CaCl_2$ + 8·0 c.c. water.
(*f*) 4·0 c.c. 0·1 M $CaCl_2$ + 6·0 c.c. water.
(*g*) 0·5 c.c. 0·001 M $AlCl_3$ + 9·5 c.c. water.
(*h*) 2·0 c.c. 0·001 M $AlCl_3$ + 8·0 c.c. water.
(*i*) 4·0 c.c. 0·001 M $AlCl_3$ + 6·0 c.c. water.

Find the least concentrations of the various salts necessary for precipitation. Compare with theory (p. 685). (The above figures are taken from Sherwood Taylor, "Elementary Practical Physical Chemistry." Oxford University Press.)

SUGGESTIONS FOR FURTHER PRACTICAL WORK

(1) Determine the gold numbers of various organic colloids.

(2) Study the adsorption of oxalic acid on charcoal, and see if it obeys the adsorption isotherm.

SUGGESTIONS FOR FURTHER READING

HEDGES, E. S. "Colloids." *Arnold*, 1931.

FREUNDLICH, H. Trans. H. S. HATFIELD. "Colloid and Capillary Chemistry." *Methuen*, 1926.

HOLMES, H. N. "Laboratory Manual of Colloidal Chemistry." *New York*, 1922.

McBAIN, J. W. "The Sorption of Gases and Vapours." *Routledge*, 1931.

QUESTION

(1) Describe the preparation of a colloidal solution of arsenic sulphide. What is the effect of the addition of electrolytes to this sol ?

(2) Classify the various types of colloidal solution. What methods indicate the heterogeneous nature of colloidal solutions ?

(3) Classify the various methods of producing colloidal solutions and give examples of each.

(4) What is meant by the gold number of a colloid ? How would you determine it ?

(5) State the Hardy-Schulze Law, and discuss it.

(6) In what ways has the study of colloidal particles enabled a determination of the Avogadro number to be made ?

(7) How may the sign of the charge on a colloidal particle be determined ? Discuss the part played by the charge in determining the stability of a colloid.

(8) Discuss the applications of colloid chemistry to qualitative and quantitative analysis.

(9) What is the essential difference between the extraction of iodine from a solution by means of chloroform and that by finely divided charcoal ?

(10) What is the Freundlich adsorption isotherm ? Show how you would verify it in any one case.

CHAPTER XVII

CATALYSIS

✱ **348. Development of the Theory of Catalysis.**—A broad definition of catalysis is "the acceleration of chemical reactions by the addition of small quantities of foreign substances to the reacting system."

It is remarkable that catalysis, which to-day plays such an important part in every branch of chemistry, including particularly the technical side of the subject, was very little investigated before 1800. Like many other branches of chemistry, its study was facilitated by the atomic theory of Dalton, and the development of stoichiometry. The use of certain catalysts, however, goes back a long time before 1800, though there was no theory of their action as catalysts. Particularly the process of fermentation has been known for centuries. The action of yeast was one of the earliest phenomena to interest men of science. The "Philosopher's Stone" and the "Elixir of Life" may both be regarded as catalysts, long sought after, but never reached. The idea of gold acting as a "ferment," a small portion engendering a much greater quantity, long precedes the Philosopher's Stone. It is found in the work of Zosimus (*ca.* A.D. 300) if not in earlier writers. One of the early references to catalysts in alchemy is given by Löwenstern in his book "Laboratorium Chymicum," the fourth edition of which was published in 1767. He refers to an alchemist, Schwerzer, who, in the year 1585, had produced an "elixir" of which "one part would tinge 1024 parts of base substances." There is, however, a long distance between this and the first definite observations of catalysis in which a catalyst was shown to be able to accelerate chemical reactions without any violation of the stoichiometrical laws.

The first catalytic reactions which were studied at all systematically were (*a*) the conversion of sulphurous acid into sulphuric acid, forming the basis of the lead chamber process for the manufacture of this acid; this was known in the eighteenth century; (*b*) the hydrolysis of an aqueous solution of starch by acids to give sugars (Parmentier, 1761, Kirchoff, 1811); (*c*) the catalytic decomposition of hydrogen peroxide by metals (Thenard, 1818); (*d*) the oxidation of combustible vapours by air in the presence of a heated platinum wire (Davy, 1817), or platinum sponge (Döbereiner,

1823). This discovery caused a great sensation, and really started the investigation of heterogeneous catalysis.

Later in the nineteenth century a large number of other catalytic reactions were discovered and investigated. Of the characteristics of catalytic action which were thus demonstrated, the one that stands out above all the rest is the fact that the catalyst is not used up in the process. Relatively large quantities of the reacting substances could be brought into reaction by the use of a small quantity of catalyst, and there appeared to be no reason why, if the presence of impurities or the possibility of mechanical loss were avoided, an unlimited quantity of the reactants could not be transformed by a finite quantity of the catalyst, however small. Further, it was found that catalytic action was specific, not every catalyst being able to bring about every reaction. A catalyst frequently could only be chosen after numerous experiments. It was also discovered that a catalyst could be rendered inactive by the presence of certain substances. This was first shown by Döbereiner and Faraday.

The name "catalyst" was first given to these active substances by Berzelius in 1835. It is to be noted that quite thirty years passed, after catalytic changes were studied thoroughly, before the phenomenon was given a name.

It was soon recognised that catalysis could fall into two, or possibly three, classes. The first is homogeneous catalysis, where the catalyst is in the same phase as the reactants. One of the earliest of catalytic reactions, the lead-chamber process of making sulphuric acid, belonged to this class. The second is heterogeneous catalysis, in which the catalyst is in another phase from the reactants. This is the more important of the two classes, and is represented in the early work by Döbereiner's experiment with combustible gases and oxygen. The third need not be classed as a new type, but it is convenient to do so. It comprises the biological catalytic processes, of which the reactions due to enzymes were very early known. The hydrolysis of starch by means of diastase from germinating barley was investigated by Irvin in 1785, and by Kirchoff in 1814. Another early example was the breakdown of amygdalin by emulsin, studied by Liebig and Wöhler in 1837.

Theories as to the cause of catalysis were not long in following the observations. In the first decade of the last century these explanations centred round thermal effects of some kind, such as local heating, or certain electrical effects. These were discarded by Döbereiner and Davy and others. A very important work on the action of nitric oxide in the lead chamber process was published by Clement and Désormes in 1806, in which they pointed out that

the nitric oxide acted as a carrier of oxygen owing to the formation of an intermediate compound, NO_2. This explanation, which is still regarded as correct, made others think that all catalytic action was possibly due to the formation of intermediate compounds, with the result that, in order to explain these reactions, all sorts of chemical compounds which could have no possible chance of existence were postulated. Faraday, however, did not agree with the formulation of compounds which had no separate existence, and which violated the ordinary chemical laws, and, being particularly concerned with the action of platinum in bringing about the combustion of a mixture of hydrogen and oxygen, proposed the adsorption theory. These two views, those of the formation of intermediate compounds and of adsorption, have held the field with few modifications ever since. It is interesting to note that the modern theory of adsorption which postulates the existence of special points on surfaces at which adsorption takes place was anticipated to a certain extent by Schweigger in 1823, who refers to the existence on the surfaces of solid bodies of "anlagenpunkter," at which catalysis commences.

The various theories of catalysis will be dealt with more fully later, but it may be said that during the nineteenth century the knowledge of the phenomenon of adsorption was so scanty that the intermediate compound theory was almost universally acknowledged to be correct, although some, such as Mercer and Playfair, looked at the question from the point of view of affinity. Mercer—known for his discovery of "mercerisation"—stated in 1842 that catalysts were substances with weak chemical affinities, so that if intermediate compounds were formed they would of necessity be rather unstable. Playfair, in 1848, extended this view, and stated that catalysts possessed additional affinity, which was added to the affinity of the reactants, and thus caused the reaction to go faster. The intermediate compound theory received further enhancement by the discovery in 1867 by Deacon of his process for the manufacture of chlorine from hydrogen chloride by passing it over heated cupric chloride in the presence of oxygen. He was actually seeking examples of catalysis involving intermediate compound formation when he came across the formation of chlorine by heating cupric chloride in air, and combined this with the regeneration of cupric chloride by heating cuprous chloride with hydrogen chloride and air.

Schönbein, in 1850, stated that no chemical reaction, whether catalytic or not, must be regarded as taking place directly according to the equation, but that each chemical process is made up of a series of elementary processes. This was a further aid to the intermediate compound theory. The introduction of a new substance

into the system in the form of a catalyst meant the possibility of new elementary processes. The theory would also explain the specific nature of catalysts, and also poisoning (§ 354).

The whole study of catalysis was put on a new footing by the work of Ostwald. In 1888 he formulated a series of criteria of catalysis, which summed up the behaviour of catalysts.

***349. Criteria of Catalysis.**—Ostwald's points are given below:

(1) *The catalyst remains unchanged at the end of the reaction.*—This only applies to the chemical composition of the catalyst. Its physical form may change completely. Thus, if coarsely powdered manganese dioxide is mixed with potassium chlorate in the preparation of oxygen, at the end of the reaction it is found to be finely powdered.

(2) *A small amount only of catalyst is required.*—This is not invariably true. Many examples are known where the catalyst must attain a definite minimum concentration before it will act. An example of this is provided by the Friedel and Crafts reaction in organic chemistry, where aluminium chloride is used to promote the reaction between an aromatic hydrocarbon, such as benzene, and an aliphatic halide, such as ethyl chloride. Here, however, it is known quite definitely that an intermediate compound is formed.[1] On the other hand, it is known that in many cases a very small amount of catalyst is sufficient for the purpose. Attempts have been made to determine the threshold concentration of catalyst required, but they have not been very satisfactory.

(3) *A catalyst alters the speed of the action, without, however, altering the final state of equilibrium.*—This is true where the catalyst is needed only in small concentration, and indeed this criterion would be required from the application of the law of conservation of energy. If, however, the catalyst is present in large quantity, there is no need for this to be true, and experiments carried out by Jones and Lapworth on the equilibrium constant of the hydrolysis of ethyl acetate in the presence of varying amounts of hydrochloric acid, which acts as a catalyst, indicate that it is not true when the amount of acid used is large.

[1] The explanation of the Friedel and Crafts reaction is expressed by the equations:—

$$XH + YCl + AlCl_3 = XHYClAlCl_3.$$
$$XHYClAlCl_3 = XY + HCl + AlCl_3.$$

It is necessary to add at least one gram-molecule of aluminium chloride to each gram-molecule of the reacting substance. It is extremely probable that the aluminium chloride is not a catalyst at all, but that the co-ordination compound formed ($XHYCl . AlCl_3$) is immediately decomposed. To return to the original theory, Böeseken has supposed that a large excess of the catalyst is required, as some is used up in the formation of the co-ordination compound, and more must be added to provide some of the *free* catalyst.

(4) *A catalyst cannot start a reaction, but only increases or decreases its speed.*—This, again, is probably not true. Many reactions are known to be initiated by a catalyst, as far as can be judged. Of course, there is always the reply to this objection that the reaction may proceed so slowly without the catalyst that its speed cannot be measured. Thus, the work of Baker on the catalytic influence of water described on p. 330, in which he showed that many ordinary chemical reactions would not take place without the presence of water, seems to provide evidence against this criterion.

350. Heterogeneous Catalysis.—This class of catalysis includes the majority of these reactions which are of commercial importance, and has been studied therefore to a much greater extent than homogeneous catalysis. In this type, the catalyst is a separate phase from the reactants, which are usually gases. The catalysts that have proved most useful in this field are the metals platinum, nickel, copper and iron, usually in a state of fine division, and certain metallic oxides, chiefly those of iron, zinc, chromium, bismuth and molybdenum. This is not, of course, an exhaustive list.

Catalysts are usually specific in their action. One catalyst may serve for an hydrogenation, whilst it would be useless for an oxidation.

Important technical processes using the phenomenon of heterogeneous catalysis are :—

(1) The preparation of hydrogen from water gas and coke oven gas. The carbon monoxide of the water gas is converted into carbon dioxide by the action of steam in the presence of ferric oxide to which a promoter (§ 353) has been added.

$$CO + H_2O = CO_2 + H_2.$$

(2) The preparation of methyl alcohol from carbon monoxide and hydrogen, using as a catalyst zinc oxide together with chromium oxide as a promoter.

$$CO + 2H_2 = CH_3OH.$$

(3) The Haber process for synthesising ammonia in which nitrogen and hydrogen in the correct proportions are passed over a heated catalyst, formerly platinum, but now mainly iron, containing a promoter.

$$N_2 + 3H_2 = 2NH_3.$$

(4) The oxidation of ammonia to form nitric oxide, and, ultimately, nitric acid.

$$\begin{gathered}4NH_3 + 5O_2 = 4NO + 6H_2O\\ 2NO + O_2 = 2NO_2\\ 2NO_2 + H_2O = HNO_3 + HNO_2\\ 3HNO_2 = HNO_3 + H_2O + 2NO\end{gathered}$$

The catalyst formerly employed was platinum wire gauze, but now the cheaper mixture of ferric and bismuth oxides has taken its place.

(5) Hydrogenations, such as the conversion of liquid oils into solid fats, as in the manufacture of margarine. The catalyst is finely divided nickel.

$$[\underbrace{X - CH = CH - Y}_{\text{Unsaturated Oil.}}] + H_2 \rightarrow [\underbrace{X - CH_2 - CH_2 - Y}_{\text{Saturated Fat.}}]$$

(6) The contact process for manufacturing sulphuric acid. Sulphur dioxide is directly oxidised by atmospheric oxygen in the presence of platinum.

$$2SO_2 + O_2 = 2SO_3.$$

(7) The removal of sulphur compounds from coal gas. Hydrogen sulphide is removed by passing the gas over ferric oxide in the presence of sawdust.

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O.$$

The other volatile sulphur compounds in the gas are converted into hydrogen sulphide by passing over a hydrogenation catalyst, *e.g.*, metallic nickel. The hydrogen sulphide is then removed as above.

(8) The use of activated charcoal. This charcoal is prepared from special woods, and is largely used in chlorinations. The liquid to be chlorinated is passed down a tower filled with activated charcoal, whilst the chlorine gas is passed up. Hydrogen chloride is now manufactured by passing a mixture of hydrogen and chlorine over activated charcoal.

Further details of these reactions will be found in text-books of Inorganic Chemistry.

351. Enzyme Catalysis.—Enzymes probably act in solution, and therefore may be homogeneous catalysts. They are complex organic compounds, which are not very stable, and form colloidal solutions with water. They catalyse numerous reactions, especially those connected with natural processes. Most of them are hydrolytic in their action, *i.e.*, they cause the addition of water to a substance. Thus, diastase converts starch into maltose, and maltase, a different enzyme, will cause the hydrolysis of maltose into glucose. Invertase converts sucrose into a mixture of glucose and fructose; and zymase converts glucose into alcohol.

The exact mechanism of the working of enzymes is not known, but they are extraordinarily important substances in the human body.

352. Mechanism of Catalysis.—It has already been stated that there are two broad theories of catalytic action, one of which may be termed the "chemical" theory, and the other the "physical" theory. The first postulates the formation of intermediate compounds, often of doubtful composition, whilst the latter supposes

that adsorption takes place. These two views have now been brought into harmony by the work of the last twenty years.

The Intermediate Compound Theory.—Intermediate compound formation may result in reactions of two types, which may be represented by the equations :

$$\text{I.} \quad AX + Ct = CtX + A,$$
$$CtX + B = BX + Ct,$$

giving
$$AX + B = A + BX.$$

$$\text{II.} \quad A + B + Ct = ABCt,$$
$$ABCt = AB + Ct,$$

giving
$$A + B = AB.$$

In these equations the symbol *Ct* stands for the catalyst.

There can be no doubt that in a very large number of cases of catalysis there is the formation of intermediate compounds. One need only quote the lead chamber process for the manufacture of sulphuric acid, which is usually regarded as a catalytic process, to show that here intermediate compound formation is necessary. Actually this is a case of homogeneous catalysis, as both the catalyst and the reactants are in the same phase, *viz.*, the gaseous phase. The production of oxygen by heating a mixture of manganese dioxide and potassium chlorate is another reaction in which compound formation is probable. This reaction has been regarded by McLeod as consisting of the following successive changes :

$$(a)\ 2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2.$$
$$(b)\ 2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$
$$(c)\ K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2.$$

This accounts for the fact that in this reaction the oxygen is often contaminated by a small quantity of chlorine, and that the residue, if a small quantity of manganese dioxide only is used, is often coloured pink.[1] There have been physical explanations of this reaction, one of which was that on heating the potassium chlorate a supersaturated solution of oxygen in potassium chlorate is obtained, which is broken up when manganese dioxide is added, just as when dust particles enter a supersaturated solution of a salt.

[1] McLeod's theory cannot be reconciled with the fact that nickel oxide, NiO, and ferric oxide, Fe_2O_3, are *quantitatively* as good catalysts in this reaction as manganese dioxide. CuO does not catalyse the reaction. These facts suggest that the reaction may be (in the case of manganese dioxide)

$$KClO_3 + 3MnO_2 = 3MnO_3 + KCl$$
$$3MnO_3 = 3MnO_2 + 3O.$$

MnO_3 has not, however, been isolated from this reaction. NiO might form a higher oxide in a similar manner. CuO could not, as no higher oxide of copper is known. McLeod's theory fails with NiO, as this substance, although a better catalyst than manganese dioxide, could not form a nickelate.

If this is true, then any fine powder should bring about the decomposition. It is a fact that some other powders do so, but it is certainly not a general phenomenon. Also, when the pressure is reduced over ordinary potassium chlorate, it does not facilitate the decomposition as it would be expected to do if the salt were a supersaturated solution.

The very fact that intermediate compound formation can take place in catalytic reactions indicates that the stability of such compounds must be small. Otherwise they would not undergo change in such a facile way. This may account for the fact that they frequently cannot be isolated. On the other hand, there are many reactions in which the presence of these compounds is ruled out on grounds of stoichiometry, and to these the adsorption theory may be applied.

The adsorption theory states that before reaction the reactants are adsorbed on the surface of the catalyst. The origin of this idea may be traced to Faraday. There is no definite chemical compound, but an " adsorption compound " of no definite composition, possibly one molecule thick, is formed at the surface. The work of Hardy, Langmuir, Adams and others on the nature of thin films has added enormously to our knowledge of adsorption. Also, our modern knowledge about the electrical structure of the atom, and the nature of chemical combination, makes it obvious that there is no essential difference between physical and chemical forces. The same forces which can hold the molecules or atoms of the catalyst together can act at its surface to attract molecules of other substances and give rise to adsorption. It is obvious that this explains very well the fact that the more finely divided the catalyst is, the better does it work. There will be greater surface and more room for adsorption to take place. For reaction to occur the two molecules which are going to react must presumably be adsorbed side by side; the new molecule is then formed and evaporates off, leaving the space clear for the next molecules to be adsorbed, and so on.

The increase in concentration which must occur in the adsorbed phase would alone account in some measure, though not completely, for acceleration of reaction. Also, the surface of a solid is often capable of taking up the energy liberated in the reaction (heat of reaction), and this may perhaps be used in enhancing chemical reactivity throughout the mass of reacting substances. If, for example, two bromine atoms collide in the gaseous phase and form a molecule, the heat of reaction, 46,000 gm.-cals. per gram-molecule, is carried momentarily by the bromine molecule. This amount of energy is comparable with the heat of activation, so that the newly formed molecule will be very likely to decompose again unless this

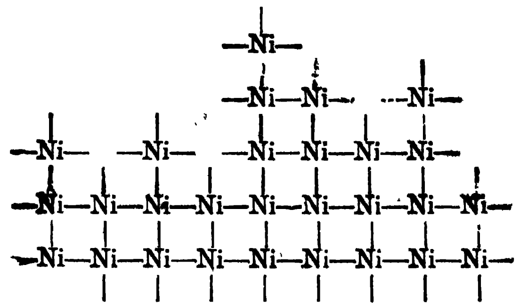
energy is given up. The presence of a third body, taking no actual part in the reaction, would help to remove this energy. The chance for a triple collision occurring in the gas phase is small, but when there is a solid surface present everywhere, the chance is much greater. It is recognised that this theory cannot be of universal applicability, since any surface ought to be capable of acting in this way.

Another point has to be considered. It can be shown that the process of activation is aided in the solid-gas interface as compared with the gas space itself. The heat of activation of a unimolecular heterogeneous reaction is approximately half that required for a homogeneous bimolecular reaction (§ 171). Thus if two molecules meet in the gaseous phase they must possess twice as much energy if they are to combine, than when they combine on the surface of some solid body present. The actual process of adsorption also liberates a certain amount of energy (heat of adsorption) which may provide some of the heat of activation. Some cases of this are known. Attempts have been made to derive a complete theory of heterogeneous catalysis on this basis.

Langmuir has made attempts to explain the mechanism of adsorption. In experiments on the nature of films of fatty acids on the surface of water, he came to the conclusion that the molecules of fatty acid in the film were oriented in a certain direction, the carboxyl ends being attracted towards the water, and the hydrocarbon chains repelled from it. He argues that the adsorption of a gas by a solid probably entails a similar orientation. Also, on adsorption, the molecules may be deformed, *i.e.*, the distribution of their electric fields may be different from before. This deformation may give rise to the development of additional energy at certain parts of the molecule, thus enhancing its activity at those parts. According to Langmuir, the only difference between adsorption and compound formation lies in the strength of the binding. In compound formation one reactant is powerful enough to break down the lattice of the other, and together they form a new lattice. In adsorption, the amount of energy involved is too small to do this. These views have been largely developed by H. S. Taylor, Mittasch and Willstätter, the latter with particular reference to enzyme catalysis. It is seen that the two ideas of catalytic processes, first, the formation of intermediate compounds, and, second, the adsorption theory, both find a place in these new explanations.

It is also known that catalytic activity is not uniformly distributed over the surface of a catalyst. There appear to be active spots. Catalysts have been examined by X-ray methods and shown to possess a crystalline structure, but on the surface the catalyst will

be uneven. If we represent the surface of a nickel catalyst as follows:



the lines representing the chemical forces acting between the atoms, and not standing for valency bonds, it is obvious that at the peaks there will be a greater number of unsatisfied forces, which can be used to attach molecules. Isolated nickel atoms would be centres of great activity. This explains the fact that the activity of a catalyst depends a good deal on its method of preparation and is enhanced when the surface is increased. Hence the great catalytic activity of such substances as platinum black.

353. Promoters.—The activity of a catalyst is frequently enhanced by mixing it with some other substance, not necessarily itself a catalyst. This action is called "promoter" action. Thus, in the Haber process for the synthesis of ammonia, it has been found that mixed catalysts of the composition $Fe + Al_2O_3 + K_2O$ are particularly active; in the oxidation of ammonia, iron oxide and bismuth oxide may be used; and the synthesis of methyl alcohol from carbon monoxide and hydrogen is well catalysed by zinc oxide mixed with chromium oxide or other oxides as promoters. No definite theory can be put forward concerning these facts. The action may resemble the phenomenon of photo-sensitisation in the case of photochemical reactions (p. 725), but at present our knowledge is too empirical in nature to enable us to draw definite conclusions.

354. Poisoning of Catalysts.—Very frequently the presence of small quantities of impurities in the reacting substances will render the catalyst useless. These are called "catalyst poisons." It is a remarkable fact that substances which poison catalysts are usually also poisonous to organisms. Thus arsenious oxide and hydrogen cyanide are two of the most powerful of catalyst poisons. The poison may be specific. The amounts of various poisons necessary to reduce the velocity of decomposition of hydrogen peroxide to one-half of its original value have been determined, when the reaction has been catalysed by colloidal platinum and by

hæmase (an enzyme present in blood). The results are embodied in the Table below.

TABLE CXVI.—CONCENTRATION OF POISON REQUIRED TO REDUCE THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE TO ONE-HALF

Poison.	Catalyst. Concns. in gm.-mols./litre.	
	Colloidal Pt.	Hæmase.
Hydrogen cyanide	5×10^{-8}	1×10^{-6}
Mercuric chloride	5×10^{-7}	5×10^{-7}
Hydrogen sulphide	3×10^{-6}	1×10^{-6}
Carbon monoxide	very poisonous	no poisoning
Aniline	2×10^{-4}	$2{\cdot}5 \times 10^{-3}$
Hydrogen chloride	3×10^{-4}	1×10^{-5}
Iodine in potassium iodide	2×10^{-7}	2×10^{-5}

It is seen that the poisons do not affect the two catalysts in the same degree. It is clearly very necessary to prevent poisoning of catalysts on the technical scale.

The effect of poisoning is probably a reduction of the number of active spots. All the poisons are very highly adsorbed (a fact which also explains, in part, their poisonous action to the human body), and will therefore quickly cover the active centres and render the catalyst useless. The poisoning is not always permanent. If the poison is held only on the surface by adsorbing forces, it may be removed again if circumstances are favourable. On the other hand, poisons frequently form chemical compounds with the catalyst. Particularly is this so with hydrogen sulphide and the metal catalysts.

Poisoning is not altogether an evil, and may sometimes be useful. In organic reactions it is sometimes necessary to stop the reaction at a certain stage, and this can be done by addition of a certain amount of a specific poison which will prevent the catalyst from reacting past a certain point.

Frequently reactions can be slowed down by the addition of some foreign substance, which is then sometimes referred to as a *negative catalyst*. Actually, however, it is usually a case of poisoning of a catalyst already present. Thus the oxidation of benzaldehyde by the air is known to be catalysed by the surface of the glass vessel in which it is contained. The addition of a small quantity of hydroquinone stops this oxidation. Hydroquinone itself, however, is not

a negative catalyst, but is preferentially adsorbed by the glass surface and poisons it. This explanation applies in the majority of cases of so-called negative catalysis.

An interesting theory has been developed by Warburg. Bredig suggested that the colloidal metals might be regarded as inorganic ferments, and Warburg suggests that finely divided charcoal may be regarded as a model of the breathing cell, for amino-acids are oxidised at its surface by free oxygen, as they are in the living cell. Warburg has made a study of the surface of catalytically active charcoal, prepared from blood, and containing iron and nitrogen. He has shown that the "breathing" of this model cell can suffer a type of narcosis when substances such as phenylurea are added. When the narcotic is removed, the catalyst functions in its normal way once again. Hydrocyanic acid, however, poisons the catalyst. It stops its "breathing" altogether, and, whilst fairly large concentrations of the narcotic are required to induce an effect, only very small quantities of the poison are required. The oxidation of amino-acids at a charcoal surface appears to take place at certain spots on the surface in which metallic iron is present as an impurity. There is a fair amount of evidence for this view. The quantity of hydrocyanic acid necessary for poisoning is approximately equivalent to the iron content. Charcoals containing little iron are weaker catalysts than those which have been treated with iron salts. Also, the hydrocyanic acid would in all probability react with the iron producing a chemical compound which is catalytically inactive. It has been suggested that similar changes take place in human cells. The cell, it is known, contains a small amount of iron, and this may be the catalytically active substance which enables oxidation to take place. When it is removed by any means, such as poisoning by hydrocyanic acid, the cell is incapable of breathing and death ensues. Narcotic action, however, is merely the shifting of the adsorption equilibrium, and not the destruction of the active centres.

There is no doubt that adsorption plays a very great part in chemical actions, and frequently when it is not suspected. Our knowledge of adsorption, however, whilst it has progressed enormously within recent years, is still inadequate to explain these reactions fully. We must gain greater knowledge of the nature of inter-atomic forces before we can make further progress. This is being done, largely from the theoretical point of view, by means of the quantum mechanics. An explanation of catalysis has been attempted on this basis, but it cannot be given here.

355. Autocatalysis.—Frequently in the course of a reaction a substance is formed which catalyses the reaction. This phenomenon

is called "autocatalysis." An example is found in the titration of oxalic acid by means of permanganate. When the first portion of permanganate is added to warm oxalic acid solution, there is an appreciable period before it is decolorised. The second portion is, however, decolorised immediately. This is because manganous salts catalyse the reaction. They are formed when the first portion of permanganate has been used up, and the succeeding portions are therefore decolorised more rapidly.

A more striking example is found in the formation of chloric acid from potassium chlorate by adding sodium bisulphite solution. The weakly acid bisulphite liberates some chloric acid, which is an oxidising agent, and oxidises the bisulphite to the more strongly acid sodium bisulphate. This is then capable of liberating more chloric acid, and so the reaction proceeds until the whole mass froths up.

* **356. Homogeneous Catalysis.**—We shall here consider the catalytic action of hydrogen and hydroxyl ions. Acids and bases are often used in the catalysis of hydrolytic reactions, such as the saponification of esters and the inversion of cane-sugar. The catalysis here is rather different from the other types that have been mentioned, because the effect appears to be proportional to the amount of acid present. At first it was thought that the effect was proportional to the hydrogen ion concentration, since the order of the strengths of acids based on their power of catalysing the inversion of cane-sugar was the same as that based on conductivity. It has now been shown that this is not true, and that neutral salts have a marked effect on the catalysis.

Arrhenius found that the addition of potassium chloride to a solution of acetic acid increased the catalytic effect of the latter greatly. This fact he explained by assuming that the potassium chloride appropriated water to itself and removed it from the solution, thus making the acid stronger and increasing its catalytic effect. Through the work of Dawson and others, it is now known that the ions of the salt itself are effective in the catalysis. Dawson, working with the iodination of acetone, found this reaction to be catalysed by all substances which could be classified as acids or bases according to the extended theory. A fuller account of the work, together with other points affecting acid catalysis, are given in Chapter XIV., p. 595.

357. Catalysis by the Hydroxyl Ion.—Some organic reactions are known which are catalysed by hydroxyl ions. The enolic and ketonic forms of substances like ethyl acetoacetate exist together in equilibrium in ordinary specimens of the ester. The two separate forms can, however, be prepared.

$$\underset{\text{keto}}{CH_3.CO.CH_2.COOC_2H_5} \rightleftharpoons \underset{\text{enol}}{CH_3.C(OH):CH.COOC_2H_5}.$$

They rapidly change into one another, and the equilibrium is quickly attained in the presence of hydroxyl ions. The mutarotation of glucose is catalysed by these ions, as is also the condensation of acetone to form diacetonyl alcohol :

$$\underset{\text{acetone}}{2CH_3.CO.CH_3} \rightarrow \underset{\text{diacetonyl alcohol}}{CH_3.CO.CH_2.C(CH_3)_2.OH}.$$

SUMMARY

Catalysis is the acceleration of a chemical reaction by the addition to the reacting system of small amounts of foreign substances. Ostwald's criteria of catalysis were :—

(1) The catalyst remains unchanged at the end of the reaction. This is only true as regards its chemical composition.

(2) A small amount of catalyst only is required.

(3) A catalyst alters the speed of the action without altering the final state of equilibrium.

(4) A catalyst cannot start a reaction, but only increases or decreases its speed.

Most of these are only true with certain qualifications. Catalysis may be conveniently divided into three types :—

(*a*) Heterogeneous catalysis, in which the catalyst and the reactants are in different phases, *e.g.*, the Contact Process for the manufacture of sulphuric acid. Many important technical processes use this phenomenon, which frequently depends upon adsorption. The surface of the catalyst possesses a number of active points at which adsorption takes place. These are points where the normal valency forces are unsatisfied.

When a molecule is adsorbed, the electric field accompanying it is distorted and hence there is an alteration in the distribution of its energy. When molecules of the two reactants are adsorbed on adjacent spots, combination occurs and the products then leave the surface, making it free for further atoms or molecules to be adsorbed.

The other theory of heterogeneous catalysis is the "intermediate compound theory," which supposes the formation of a compound between the catalyst and one of the reactants, the compound then reacting with the other substance to give back the catalyst and the final product.

(*b*) Homogeneous catalysis, brought about by substances in the same phase as the reactants, *e.g.*, the hydrolysis of an ester with "hydrogen ions" as a catalyst.

(*c*) Enzyme action, usually hydrolytic.

In heterogeneous catalysis the catalytic effect of a substance may sometimes be greatly enhanced by the addition of another substance, not in itself a catalyst. Such substances are called "promoters"; the theory of their action has not yet been fully worked out. The poisoning of catalysts is due to the blocking of the active adsorbing spots by a substance which is very powerfully adsorbed. Although frequently to be avoided, it is occasionally useful, *e.g.*, in the prevention of the cata-

lytic oxidation of benzaldehyde, by addition of hydroquinone. So-called "negative catalysis" is usually to be attributed to catalyst poisoning.

SUGGESTIONS FOR PRACTICAL WORK

Experiment 44.—To determine the effect of a catalyst on the rate of a chemical reaction.

A good reaction to study is that recommended by Sherwood Taylor ("Elementary Practical Physical Chemistry," p. 67), *viz.*,

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2.$$

This reaction is not termolecular, as indicated by the equation, but is bimolecular. It is catalysed by cupric or ferrous ions. The rate of the reaction is conveniently studied by taking out portions from time to time and titrating against standard thiosulphate. This gives the amount of iodine liberated.

Make up a solution of potassium persulphate 0·05 molar, and one of potassium iodide 0·1 molar. The reaction should be carried out at room temperature. Mix 50 c.c. of the persulphate, and 50 c.c. of the iodide, and 20 c.c. of water. Note the time of mixing, and withdraw 10 c.c. at a time at intervals of five minutes and titrate with $N/50$ thiosulphate. Note the time of removal as that when the first drop of thiosulphate is added. See whether the results fit the bimolecular equation, and calculate a value for the velocity constant.

Now repeat the experiment using instead of the 20 c.c. of water 20 c.c. of 0·5 per cent. solution of copper sulphate.

In calculating the amount of iodine, calculate the amount formed by the action of the copper sulphate on the iodide and subtract that from the amount titrated.

See whether the bimolecular equation still holds, and calculate the new velocity constant.

SUGGESTIONS FOR FURTHER PRACTICAL WORK

Study the effect of the following substances as catalysts on the mutarotation of glucose:

(1) N Potassium chloride.

(2) $N/10$ Hydrochloric acid.

(3) N sodium acetate, approximately neutralised by addition of $N/20$ acetic acid.

SUGGESTIONS FOR FURTHER READING

SABATIER, P. "Catalysis in Organic Chemistry." *Library Press*, 1923.

RIDEAL, E. K. and TAYLOR, H. S. "Catalysis in Theory and Practice." *Macmillan*, 1926.

QUESTIONS

(1) What is meant by the term "catalysis"? What criteria of catalytic behaviour have been laid down? Discuss their applicability.

(2) Write an account of water as a catalyst.

(3) Discuss the work on catalysis by hydrogen ions and by neutral salts.

(4) What mechanism can be ascribed to heterogeneous catalysis?

CHAPTER XIX

PHOTOCHEMISTRY

358. The Absorption of Light.—Photochemistry concerns itself with reactions which are accompanied by the absorption or emission of light, the term " light " being used in its widest sense to include all radiation.

When light falls on any body, part of it is reflected, part may be transmitted, and part may be absorbed. The principles of energy demand that *only the absorbed light should be effective in bringing about chemical action.* This was established by Grotthus on theoretical grounds in 1818, and confirmed by Draper in 1839 by experiment. It is usually called the *Grotthus-Draper Law.* The converse of the Law is not true. All absorbed light does not bring about chemical action. In many cases light is absorbed without any apparent chemical effect. Thus light is strongly absorbed by solutions of potassium permanganate over certain spectral ranges, but no chemical effect is noticed. The energy thus absorbed is converted mainly into thermal energy. We shall also discover later that the light causing a reaction need not be absorbed by the substance itself, but by another in the vicinity of the substance which undergoes change, the absorbing body being itself chemically unaffected. This occurs in the phenomenon known as sensitisation (p. 725).

359. Fresnel's Reflection Law.—It was shown by the physicist Fresnel, that the proportion of the incident monochromatic light reflected by a surface perpendicular to the incident beam is given by

$$\left(\frac{n-1}{n+1}\right)^2 I_t = KI_t,$$

where I_r and I_t are the intensities of the reflected and incident light respectively, and n is the refractive index of the reflecting medium for light of the wavelength used. Since n is a constant for constant wavelength and medium, the fraction $\left(\frac{n-1}{n+1}\right)^2$ may be written as a constant, K.

The amount of light which penetrates into the medium must be $I_t - I_r$. Not all of this passes right through. Some is absorbed, and only a fraction is therefore transmitted. The proportion of

light absorbed is given by two laws, the first Lambert's Absorption Law and the second Beer's Law.

360. Lambert's Absorption Law.—Lambert, in 1760, found that layers of equal thickness of a homogeneous absorbing medium absorb equal proportions of the penetrating radiation. Consider a thin layer of the medium of thickness dx. If the light incident upon it is I_d, an amount of light dI_d will be absorbed, and according to the Law this is proportional to I_d.

$$\frac{dI_d}{dx} = -\kappa I_d.$$

On integration this gives

$$\log_e I_d = -\kappa x + c.$$

When $I_d = I_i$, $x = 0$.

$$\therefore \quad c = \log_e I_i$$

$$\therefore \quad I_d = I_i \,.\, e^{-kd}$$

where d is the thickness.

This is the mathematical expression of the Law. κ is called the "absorption coefficient." It is clear that the absorption depends on the number of molecules present. In layers of equal thickness there will be an equal number of molecules, which will absorb equal fractions of the light.

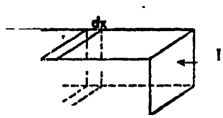


Fig. 204.

Bunsen, instead of using the absorption coefficient, used the extinction coefficient α, which is the reciprocal of that layer thickness, expressed in centimetres, at which I_i has fallen to one-tenth of its original value. It is an easy exercise to show that

$$\alpha = 0{\cdot}4343\kappa.$$

361. Beer's Law.—This extension of Lambert's Law was put forward in 1852. The Law states that the degree of absorption of light depends on the thickness, d, of the layer traversed, and on the molecular concentration in that layer. Thus a layer of gaseous chlorine 20 cm. long at a pressure of 0·1 atmos. should possess the same transmission as a 10 cm. layer where the chlorine pressure is 0·2 atmos., a fact demonstrated experimentally by von Halban in 1922. The Law can be expressed mathematically in the form

$$I_d = I_i e^{-k'cd}$$

or,

$$I_d = I_i \times 10^{-\alpha cd},$$

where

$$\alpha = 0{\cdot}4343k'.$$

The constant k' is the molecular absorption coefficient, whilst α is

the more frequently used molecular extinction coefficient. The latter is the thickness in centimetres of a layer of a molar solution which will reduce the intensity of light passing through it to one-tenth of its original value.

Beer's Law has a number of exceptions. It is usually found that at high concentrations the substance absorbs more strongly than the equation requires.

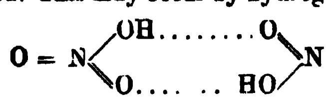
The extinction coefficient, α, varies a great deal from substance to substance and also with the wavelength of the light used. If white light is allowed to fall upon a coloured transparent substance and the transmitted light is viewed through a spectroscope, it is found that the light is absorbed to a much greater extent in certain spectral ranges; so much so, in fact, that there is frequently practically no light transmitted at all at some wavelengths. These places of great absorption in the spectrum are called absorption bands, and are characteristic of the substances giving them. Absorption bands may also occur in the ultra-violet, and their study is of considerable importance in connection with the elucidation of atomic and molecular structure (§ 376).

The nature and position of the absorption bands decide the colour of the substance. A substance like chlorine absorbs chiefly in the blue and violet, and so the transmitted light (when white light is incident upon it) is a mixture of all the colours from green to red. To us the substance appears yellowish-green. Bromine absorbs considerably more towards the red, *i.e.*, more green, and the vapour therefore possesses a brownish colour. Iodine absorbs strongly in the green, allowing violet and blue, and also the red end of the spectrum, to come through. Hence the vapour appears to be purple. Fluorine absorbs considerably in the ultra-violet and little in the visible, and therefore appears to us pale yellow in colour.

The absorption spectrum of a compound is closely related to its constitution, and, in fact, frequently provides useful information concerning it. The absorption spectra of tautomers are frequently different from each other. Hantzsch and others have used the method to investigate the tautomeric nature of certain organic substances. A good example of this is shown in the recent investigation of the constitution of nitric acid by von Halban. It is known that nitric acid will behave in two ways. When concentrated, it splits off an OH group and furnishes a nitro-group, NO_2, for example, to a hydrocarbon of the aromatic series, such as benzene, which can provide an H atom to combine with the OH to form water.

$$C_6H_6 + OH.NO_2 = C_6H_5.NO_2 + H_2O.$$

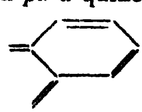
Its constitution may here be represented as $OH(NO_2)$. In dilute aqueous solution, however, it splits off a hydrogen ion and forms salts with bases. Its structure must then be of the type $H(NO_3)$. Now nitric acid absorbs in the ultra-violet and the absorption bands have been measured for the concentrated and dilute solutions of the acid. The two sets of absorption bands are quite different from each other, and therefore indicate the existence of two different forms of the acid. As the diluted acid is made more concentrated, the absorption gradually changes from the one form to the other, thus showing that there is a tautomeric equilibrium between the two forms of the acid at intermediate dilutions.

The investigation of the infra-red absorption spectra of substances is now used as a valuable method of analysis, particularly of organic compounds, such as hydrocarbon mixtures. This work has been largely developed by H. W. Thompson and his school. The infra-red absorption spectrum of nitric acid has indicated that the pure substance is associated. This may occur by hydrogen bonds between two molecules, *e.g.*,  in chains. When the acid is diluted, the intensity of the band due to the associated molecule rapidly diminishes and has almost disappeared at a concentration of 80%.

The question of absorption spectra assumes great importance when dealing with the structures of organic colouring matters. The theory of the colour of organic compounds has yet to be worked out, but a few qualitative rules have been derived as the result of the work of Witt in 1876, and of Kauffmann in 1907. An organic coloured substance must contain one or more of a certain set of unsaturated groups, called *chromophores*, of which the chief are

$$C{=}C,\ C{=}O,\ C{=}S,\ C{=}N,\ N{=}N,\ N{=}O,\ NO_2,$$

and the *ortho-* and *para*-quinonoid structures

 and 

Compounds containing these only are usually lightly coloured. The introduction of other groups into the molecule intensifies the colour and shifts the absorption bands. Thus the introduction of OH, NH_2 or CH_3 moves the absorption bands towards the red. Others shift the absorption towards the blue, *e.g.*, CH_3CO—, and C_6H_5CO—.

The absorption spectrum of a substance may vary with the solvent. Some salts have their absorption spectra widely displaced on solution in different solvents. This may be due to solvation or deformation of the electron shells in various ways owing to the polarisation of the solvents used (§ 382).

362. Application of the Quantum Theory.—The laws so far mentioned do not depend for their truth on any hypothesis concerning the nature of light; but they do not lead very far, and as soon as we desire to find out the nature of a photochemical change the necessity of knowing more of the nature of the radiation producing it is apparent. According to the quantum theory, light is not a continuous radiation; it is made up of quanta of energy, the amount of energy in each quantum being $h\nu$, where h is Planck's constant and ν the frequency of the radiation. Light cannot therefore be absorbed continuously, but only in multiples of this quantum. The number of quanta which will be absorbed by any given body will depend on the number of molecules which can absorb the light (*i.e.*, to the product of c and d, where c is the concentration and d the thickness of the layer), and upon the probability that the molecules that can absorb will be in a condition to do so. The probability term corresponds to the molecular extinction coefficient a, which, of course, varies greatly from substance to substance.

Clearly the greater the frequency of the light, *i.e.*, the smaller the wavelength (for wavelength λ, and frequency ν, are connected by the equation $v = \nu\lambda$, where v is the velocity), the greater will be the energy associated with the quantum. That is why ultra-violet light is specially active in bringing about photochemical changes. Table CXVII. gives (and Fig. 205 plots) amounts of energy associated with the quanta of radiations of various frequencies.

TABLE CXVII.—ENERGY CORRESPONDING TO VARIOUS WAVE-LENGTHS OF LIGHT

($h = 6{\cdot}548 \times 10^{-27}$ erg. secs.)

Colour.	Upper wave-length limit λ in Ångstroms.	Energy per $h\nu$, ergs.	$U = Nh\nu$ gm.-cals.
Red	7,500	$2{\cdot}62 \times 10^{-12}$	37,950
Orange	6,500	$3{\cdot}02 \times 10^{-12}$	43,740
Yellow	5,900	$3{\cdot}33 \times 10^{-12}$	48,220
Green	5,750	$3{\cdot}42 \times 10^{-12}$	49,530
Blue	4,900	$4{\cdot}01 \times 10^{-12}$	58,080
Violet	4,550	$4{\cdot}32 \times 10^{-12}$	62,580
Ultra-violet	3,950	$4{\cdot}97 \times 10^{-12}$	71,990

In column 4 the amount of energy absorbed by 1 gm.-molecule of a substance if one quantum was absorbed by each molecule is tabulated. In calculating the above figures, the velocity of light is taken as 3×10^{10} cms. per sec., and N, Avogadro's Number, as $6{\cdot}06 \times 10^{23}$. One gm.-cal. is equal to $4{\cdot}184 \times 10^{7}$ ergs (p. 188).

Since the illuminating power of a source is measured in candle-power, the latter being defined as the illuminating power given by a standard source, it is useful to know how many quanta per second correspond to the light of a standard candle. This will, of course,

vary with the wavelength of the light used. For this purpose, Gerlach found the amount of energy falling on a surface of area 1 sq. cm. at 1 metre from a standard lamp, and worked out the energy per second associated with one candle-power. This amount of energy, which came out to be 947 ergs per sq. cm. per sec., or $22 \cdot 6 \times 10^{-6}$ gm.-cals. per sq. cm. per sec., is called the "energy candle-power." The number of quanta per second, of light of any wavelength comprised in one energy candle-power can be found, since the energy of one quantum is $h\nu$.

363. Consequences of the Absorption of Light.—When light is absorbed by a system, one or more of several phenomena may occur. The absorption of light means the absorption of energy, and hence

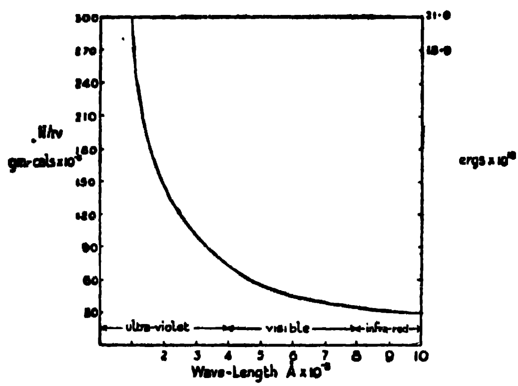


FIG. 205.—Connection between Wave-length and Energy of Quantum.

the primary effect in all photo-processes is either an increase in the thermal energy of the system or a raising of the electrons in the atoms or molecules composing the system to higher energy levels (a process known as activation, or electronic excitation). The first of these possibilities is not of great importance when the effects of visible light are being considered. Here it is the second effect which is predominant.

Photo-processes may be considered under two heads: (*a*) photo-physical processes; (*b*) photochemical processes. All photo-processes which do not involve chemical change belong to the first class. When light is absorbed by a body, if it has sufficient energy it will be able to raise certain electrons of the atoms, not only through one or two energy levels, but to eject them completely, thus ionising the atoms. This effect is known as the *photo-electric effect* (§ 365). If the light absorbed is not sufficiently energetic to remove an electron completely it will raise it to a higher energy

level, from which it may return to its normal state, either directly or in steps, with emission of energy in the form of light.

This re-emission may be either instantaneous (*fluorescence*) or after a time lag (*phosphorescence*). The energy may, however, be stored by the atom and used for bringing about chemical reactions (*photochemical reactions*), the fluorescence or phosphorescence effects being absent. These facts may be summarised as follows :—

Atom + light energy

Electrons transferred to higher energy levels.

Ionised atom + electron (removed completely)—*photo-electric effect.*

Revert to normal state instantaneously —*fluorescence.*

Revert to normal state after time lag— *phosphorescence.*

Revert to normal state after causing or entering into chemical action— *photochemical reaction.*

364. Photophysical Change.—We may include under this heading such phenomena as the photo-electric effect, fluorescence, and phosphorescence. Although not strictly chemical phenomena, the chemist must have some knowledge of them, and reference to them here is therefore not out of place.

In dealing with the effects produced by light absorption it is well to realise that whilst the primary effects may be simple, yet these are frequently masked by the occurrence of secondary changes, often of a much more complicated nature. Hence it is that many of the simple laws underlying photochemical and photophysical processes are completely masked, and are therefore difficult to verify. The same behaviour has already been noted in connection with orders of reaction. Whilst we know the simple laws which underlie uni-, bi- and termolecular reactions, we find it difficult to point to many reactions which obey these laws. Thus, only a dozen or so reactions out of the hundreds tested obey strictly the bimolecular law. All the rest are complicated by secondary reactions. Eggert has pointed out that the same is true of electrolysis. Faraday's laws underlie this phenomenon, but in many cases they fail to cover

the facts owing to secondary changes. We must be prepared for this in the study of photochemistry.

365. Photo-electric Cells.—Light has a peculiar effect on the alkali metals. It was discovered by Hallwachs as far back as 1888 that when light (and particularly the ultra-violet) is allowed to fall on an alkali metal, electrons are given off from the surface of the metal. He did not state his observations in these terms, but that is what actually happens. A type of photo-electric cell is represented in diagrammatic form in Fig. 206. The evacuated glass vessel, g, has a mirror of potassium (or some other alkali metal) on one side of its interior. The vessel is also provided with a platinum wire ring. The connections are made through the glass as in the diagram, a

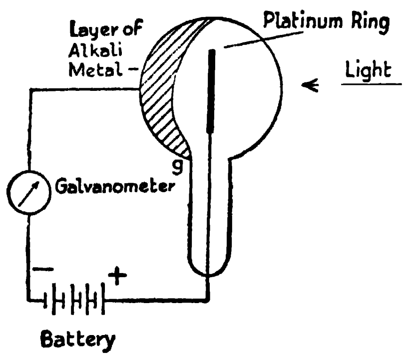


FIG. 206.—Photo-electric Cell (diagrammatic).

sensitive galvanometer and a battery being connected in the circuit. On exposing the cell to light, a current is observed to flow through the circuit owing to the passage of electrons from the alkali metal to the ring, and it is found that (under suitable conditions)[1] the strength of the current is proportional to the intensity of the light.

Of course, photo-electric cells have been greatly improved since their inception, but the principle upon which they work is shown by this simple type. It has been found that the quantum theory provides a very satisfactory explanation of the effect. Millikan, working with a lithium cell, found the e.m.f. it was necessary to apply to oppose the photo-electric current and reduce it to zero. He determined this voltage for light of various wavelengths, and it was found that when the limiting voltage was plotted against the

[1] The current strength is only proportional to the light intensity under special circumstances: (*a*) The cell must be evacuated (not a so-called gas-filled cell). (*b*) The applied voltage must be high enough to ensure that the current is saturated, *i.e.*, that all emitted electrons are caught by the ring.

frequency of the light, a straight line graph was obtained (Fig. 207). If it is assumed that one quantum of light liberates one electron, the energy with which the electron is emitted, Ve, must be equal to the energy of the quantum, $h\nu$.

$$Ve = h\nu$$

where V is the potential under which the electrons are emitted and e is the charge on the electron. In making this equality we have made the assumption that no work is done by the electron in escaping from the surface of the metal ("Austrittsarbeit"). In general, this amount must be taken into consideration. Let us call it β. Then

$$Ve = h\nu - \beta.$$

The values of h and of β can be found from the curve drawn in Fig. 207. Taking, for example, the point A where the opposing potential

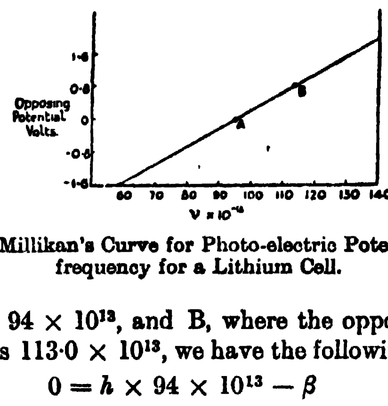


FIG. 207.—Millikan's Curve for Photo-electric Potential against frequency for a Lithium Cell.

is zero and ν is 94×10^{13}, and B, where the opposing potential is 0·8 volts and ν is $113{\cdot}0 \times 10^{13}$, we have the following equations:

$$0 = h \times 94 \times 10^{13} - \beta$$

$$0{\cdot}8 \times 4{\cdot}77 \times 10^{-10} = h \times 113{\cdot}0 \times 10^{13} - \beta.$$

Subtracting the first equation from the second and dividing by 300 to bring the volts into electrostatic units (p. 57), we have

$$h = \frac{0{\cdot}8 \times 4{\cdot}77 \times 10^{-10}}{(113{\cdot}0 - 94{\cdot}0) \times 10^{13} \times 300} = 6{\cdot}69 \times 10^{-27}.$$

This agrees very well with the actual value of the Planck constant derived by many other methods ($6{\cdot}548 \times 10^{-27}$ erg-seconds). β can be derived similarly, and comes out to be $6{\cdot}2 \times 10^{-12}$ erg.

What happens in the photo-electric process is that ionisation is produced by the absorption of energy. By the absorption of one quantum the valency electron (p. 156) is completely removed from the atom.

When certain substances are illuminated, it is found that their electrical conductivity is increased. This was first discovered for

the element selenium, and the effect was made use of in the selenium cell. But selenium is not the only element that shows the effect, and many crystalline substances (all with a refractive index over 2, and therefore with high electronic deformation (§ 380)) also come into this class. The theory of photo-conduction has not been fully worked out. Probably what happens is that by the action of light electrons are loosened in the space lattice, and on application of a field are capable of migrating through the substance to the electrodes, just as the electrons in a metal (§ 268). The experiments of Gudden and Pohl show that for every quantum absorbed, one electron is set free.

The commercial application of photo-electric cells is most important and interesting, but there is no space to deal with it here in detail. Talking pictures are made possible entirely by the photo-electric effect. The operation of electrical apparatus by light rays at a distance, as in burglar alarms, etc., makes use of photo-electric cells. The discovery of these phenomena ranks next in importance to that of the wireless valve from the point of view of practical application.

366. Fluorescence.—Fluorescence may be regarded as a secondary effect consequent upon the primary process of absorption of a quantum of light by an atom or molecule. In fluorescence, light is absorbed at a certain wavelength and emitted at a greater wavelength. This fact was discovered by Stokes in 1852. There are but few exceptions to this law, and they can be readily explained (see below). Fluorescein and eosin are stock examples of fluorescent substances, but the phenomenon is shown by a very large number of compounds (including inorganic compounds, such as uranyl sulphate $UO_2 . SO_4$), and frequently also in the ultra-violet, so that the fluorescence is invisible. What happens in this process? The molecule absorbs a quantum of energy $h\nu$. This quantity is sufficient to raise an electron to a higher energy level, but not to eject it completely. The electron returns to its original level by steps, going through intermediate orbits. Since these jumps are none of them of such great energy value as the original jump, the wavelength of the emitted light must be greater than that of the absorbed light.

A very interesting case of fluorescence which explains the few exceptions to Stokes' rule was discovered by Franck and Cario in 1923. Mercury vapour absorbs light of wavelength 2536 Å., but is not ionised by it. The vapour merely "glows" with that light —the light is emitted at the same wavelength as that at which it was absorbed. This process is called "resonance," and is analogous to acoustical resonance. If mercury vapour is mixed with the

vapours of silver, lead, sodium or thallium, and is then irradiated with light of wavelength 2536 Å., the vapours of the foreign metals fluoresce. Franck called this "sensitised fluorescence." He showed that when a quantum is absorbed it merely adds itself to the energy already inherent in the molecule as thermal energy, and enables electrons to be raised to higher energy levels than would be possible with the quantum alone. Thus, we can, in a few cases, induce fluorescence of shorter wavelength than that of the absorbed light, since the energy emitted is not only that of the absorbed quantum, but also that inherent in the system before the absorption.

367. Phosphorescence.—Fluorescence is instantaneous. As soon as the light is absorbed, fluorescence commences, and, as soon as it is cut off, the fluorescence ceases. When we say instantaneous, we mean that the time interval between the two events is not greater than 10^{-6} sec. In the case of phosphorescence a substance, after absorbing light, continues to emit light of another wavelength for some time afterwards. Numerous phosphors can now be made by preparing intimate mixtures of sulphides of the alkaline earth metals with about 2·5 per cent. of alkali chloride, and a trace of the sulphide of a heavy metal. Phosphorescence is best looked upon as slow fluorescence. It is found mainly in solids, as might be expected owing to the greater difficulty of motion. It is found that if fluorescent substances are fixed by fusion with, say, boric acid and cooling, the masses thus formed phosphoresce.

368. Photochemical Reactions.—It has already been stated (§ 363) that when light is absorbed by an atom or molecule the primary change is the formation of an excited atom or particle :

$$A + h\nu = A^*$$

where A^* represents excited A. This is to be regarded as the primary process in all cases, whether photophysical or photochemical.

As regards primary chemical changes, Einstein assumes, in accordance with the above, that *each molecule entering into reaction has to be excited by the absorption of one quantum of radiation.* This is known as the *law of the photochemical equivalent.* It is necessary to emphasise once again that it applies only to the primary process, and that, in general, secondary processes take place quite independent of the light reaction, and may completely mask the energy change of the primary process. The *quantum efficiency,* γ, of a reaction is the number of molecules actually decomposed per quantum of radiation absorbed. It is sometimes called the *photochemical yield.*

A very great number of photochemical reactions have been studied, and most books on the subject are more or less a collection of the facts with little attempt at systematisation, for it is exceedingly difficult to embrace the many facts in one system. We may, however, classify photochemical reactions roughly into the following classes (after Eggert) :—

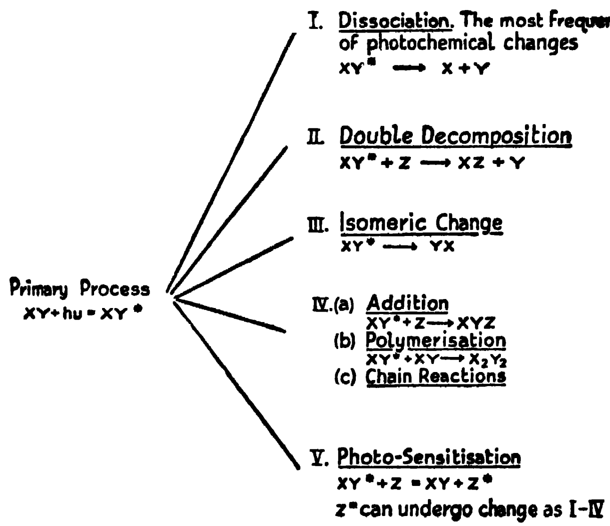


FIG. 208.—Photochemical Processes.

Examples of these various classes will be taken. The velocity of any chemical reaction is the speed at which the slowest stage of it takes place. Now in all probability the excitation of the atom or molecule by the absorption of a quantum is the most rapid part, for it has been shown that the time taken for excitation, if the quanta are available, is less than 10^{-9} second. The speed of the reaction will therefore be dependent largely upon the subsequent chemical reactions.

369. Examples of Secondary Processes.—(1) *Dissociation.*—This is by far the most common type of secondary reaction in photochemical processes.

The decomposition of hydrogen bromide and hydrogen iodide has been investigated by Warburg (1916). It was found that two molecules of gas were decomposed by a single quantum of light energy. Warburg explained this by assuming that the primary photochemical absorption of a quantum led to formation of atoms of both hydrogen and bromine.

$$HBr + h\nu = H + Br.$$

This is followed by the secondary change

$$H + HBr = H_2 + Br$$

and halogen molecules are then formed from the atoms by recombination,

$$Br + Br = Br_2.$$

There is another explanation. Stern and Volmer (1922) have pointed out that the absorption of light energy might give rise to an energy-rich form of the hydrogen bromide, which on collision with an ordinary inactive molecule could cause decomposition as follows:

$$HBr + h\nu = HBr^*$$
$$HBr^* + HBr = H_2 + Br_2.$$

Experiments on the absorption spectra of the halogen hydrides are in favour of Warburg's theory.

A very important reaction falling into this class is the formation of the latent image in photography. Radiation is capable of breaking up the silver halides into their elements. In this case, however, we are dealing with a reaction in the solid state and not one taking place in the gaseous phase. The process is represented as

$$(AgBr)^* = Ag + Br.$$

If the silver halide is exposed to light it turns grey in time, owing to the formation of free silver and free bromine. Why does this reaction take place? It has been shown that the silver halides form an ionic lattice, such as that found in sodium chloride. It is a well-known fact that fused silver chloride will conduct, the electrolysis of fused silver chloride being used for the preparation of pure chlorine. Now an ionic lattice means that the bromine ion in the silver bromide is much more loosely held than in an ordinary molecular lattice. Substances with ionic lattices are more or less easily affected by light. Thus coloured rock-salt can readily be prepared by irradiation of rock-salt crystals with ultra-violet light, the colour being due to the formation of free sodium. In the case of silver bromide it is thought that excitation of the bromide ion first takes place with liberation of free bromine and an electron. The electron then neutralises the silver ion and gives free silver:

$$(Br^-)^* = Br + \epsilon$$
$$Ag^+ + \epsilon = Ag.$$

In photography this process is not carried to completion. In

some way the few silver particles formed are able to break down the silver halide in their neighbourhood catalytically when treated with an organic reducing agent (the developer). The theory of this process is still in doubt.

The majority of photochemical dissociation reactions do not give a quantum efficiency agreeing with Einstein's Law.

(2) *Double Decomposition.*—The action of bromine on hexahydrobenzene, C_6H_{12}, when illuminated by light of wavelength 4760 Å., gives mono-bromhexahydrobenzene and hydrogen bromide.

$$C_6H_{12} + Br_2 = C_6H_{11}Br + HBr.$$

The reaction was investigated by Nernst and Pusch, who found $\gamma =$ 1·1, and by Noddack, using light of wavelength 4690 Å., who found $\gamma = 1{\cdot}0$.

The action of water on monochloracetic acid is another example of such a reaction,

$$CH_2Cl.COOH + H_2O = CH_2OH.COOH + HCl.$$

The quantum efficiency in most of these simple interchange reactions is found to be approximately 1·0, as required by Einstein's Law.

(3) *Isomeric Transformation.*—This was investigated by Warburg in 1912 with the conversion of maleic into fumaric acid and the reverse reaction, by exposing their aqueous solutions to light of wavelength 2070 Å., 2530 Å. and 2820 Å.

$$\left(\begin{array}{l}H.C.COOH\\ H.C.COOH\end{array}\right)^{*} = \begin{array}{c}H.C.COOH\\ \|\\ COOH.C.H\end{array}$$

and

$$\left(\begin{array}{c}H.C.COOH\\ \|\\ HOOC.C.H\end{array}\right)^{*} = \begin{array}{c}H.C.COOH\\ \|\\ H.C.COOH\end{array}$$

Neither of these reactions obeys Einstein's Law. It was found that in the formation of fumaric from maleic acid 0·03 molecule was transformed per quantum, for light of wavelength 2070 Å., whilst in the reverse process it was 0·11.

It is clear that as both the forward and the reverse reactions are brought about by the absorption of light, a state of equilibrium will ultimately be reached, when as much fumaric is converted into maleic acid, as the reverse. Such an equilibrium is called a "*photo-stationary state.*" The position of the equilibrium can be calculated from a knowledge of the quantum efficiencies of the forward and the

reverse reactions. In this case the equilibrium mixture is found to contain approximately 75 per cent. of maleic acid. The low quantum yields in this photochemical reaction have been explained by Warburg by supposing that the primary action of the light is to separate the molecules into two portions which can then re-unite. Some of them combine to give the isomer, whilst others give the original molecule again. The probability of the latter process is supposed to be considerably greater than that of the former.

(4) *Polymerisation*—a special case of addition. This is illustrated by the polymerisation of anthracene $C_{14}H_{10}$, to dianthracene, $C_{28}H_{20}$, in solution (benzene, toluene and xylene have been used as solvents). This reaction was investigated by Luther and Weigert (1905), who found that the polymerisation was reversed in the dark, the dianthracene depolymerising to form anthracene. This reaction goes practically to completion in the dark.

$$2C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} C_{28}H_{20}$$

When a solution of anthracene in benzene is illuminated, these two reactions go on together ; polymerisation occurs under the influence of the light, and depolymerisation owing to the thermal effect. When the rates of these two reactions become equal, a photo-stationary state is reached. The value for the quantum efficiency given by Weigert is 0·48, when the wavelength of light used was 3660 Å. It is clear, then, that the Einstein Law is not obeyed, and that the primary process is not so simple as that outlined above. Similar results have been obtained by Weigert and Kruger (1913) with methylanthracene.

Further examples of addition are provided by the photo-chemical action of carbon monoxide on chlorine (quantum efficiency 1,000–1,500), which is briefly referred to under chain reactions ; the combination of hydrogen and chlorine (§ 370), etc.

(5) *Sensitisation.*—As in the case of sensitised fluorescence, the substance which undergoes change in a photochemical process need not necessarily be the absorbing molecule. There may be present something else which does not undergo change, but merely absorbs the energy, and then hands it on to the substances that will react. This process is called *photo-sensitisation*, and is of very great importance.

One of the most important photo-chemical processes is that which goes on in nature every day, *viz.*, the building up of carbo-hydrates in plants from carbon dioxide and water in the presence of light. The reaction expressing the change is

$$xCO_2 + yH_2O = C_x(H_2O)_y + xO_2.$$

It was at first assumed that formaldehyde was the original product

$$CO_2 + H_2O = HCHO + O_2,$$

and that this polymerised to carbohydrates. This reaction can be brought about on the laboratory scale, but only very small quantities of carbohydrates are produced. It has been claimed that the production of formaldehyde from carbon dioxide and water under the influence of ultra-violet light has been demonstrated ; but even if this can be done in the laboratory, it is quite uncertain whether this can be the mechanism of the reaction in the case of plants, as formaldehyde is a plant poison.

Carbon dioxide and water absorb only in the ultra-violet, as they are colourless. It is thought that their photochemical combination is photo-sensitised by chlorophyll, the green colouring matter of plants. This substance absorbs in the visible, and appears to be able to hand on the energy thus gained to the carbon dioxide and water molecules, causing them to combine even in the absence of ultra-violet light. This is the simplest explanation of the reaction of which the mechanism is not definitely known. Many more complicated explanations have been put forward, in which the chlorophyll plays a definite chemical part ; the best of these appears to be that the chlorophyll combines with carbon dioxide in the presence of an enzyme to give water, carbohydrates and dehydrogenated chlorophyll. This is a "dark" reaction. The dehydrogenated chlorophyll then undergoes a photochemical reaction with water, re-forming chlorophyll, and oxygen is evolved. This theory agrees with the majority of the facts discovered about photosynthesis, and explains why the irradiation of a mixture of carbonic acid and chlorophyll with ultra-violet light under laboratory conditions does not produce a carbohydrate. The enzyme (provided in nature by the plant) is absent.

Another extremely important process based on photo-sensitisation is the use of the cyanine dyes in the manufacture of photographic plates. An ordinary photographic plate is much more sensitive to light of short wavelength than to light of longer wavelength (*e.g.*, the red). It is found, however, that if a small quantity of a special dyestuff is incorporated with the halides in the making of the emulsion, there is a much more even spectral sensitivity. This is due to the fact that the dyestuff absorbs light much more regularly over the visible spectrum than does the halide mixture alone, and it is able to hand on the energy thus gained to the halides and reduce them just as if they themselves had absorbed the light. These plates, which are considerably more sensitive over the whole spectrum range, are called "panchromatic" plates. They are

sensitive even to the red light that is used in dark rooms, and so must be worked in complete darkness.

370. Chain Reactions.—One of the fastest reactions known is the photochemical combination of hydrogen and chlorine in the presence of a small quantity of water vapour.[1] This reaction is explosive when the system is exposed to ultra-violet light, and experiment shows that the photochemical yield (p. 721) may be as great as 10^6, though it decreases greatly as the pressure is decreased. This reaction has been very exhaustively studied, and it has been found that there is an induction period before reaction takes place which varies with the experimental conditions. This appears to be due to the presence of impurities, which are removed by the chlorine before combining with the hydrogen. It has also been discovered that the presence of oxygen exerts an inhibitory effect, and that water vapour is necessary if the reaction is to take place in visible light.

Any satisfactory explanation of the process must take all these facts into account, but at the moment none is forthcoming. Nernst (1916, 1918) supposed that the absorbed light first brought about decomposition of the chlorine molecules into atoms, and that then a chain of reactions took place. The photochemical reaction therefore merely starts off the chain.

$$\begin{aligned} Cl_2 + h\nu &= 2Cl \\ Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl. \end{aligned}$$

The two secondary reactions are both accompanied by a decrease in the free energy, and hence will occur spontaneously. The chain of reactions will go on until the hydrogen or chlorine atoms are removed in some way, such as by formation of molecules.

There is a considerable amount of evidence in favour of this view: (1) if some substance could be added to the system to remove chlorine or hydrogen atoms, the chain would be broken. (2) Marshall and Taylor have shown that at least one step in the chain can be carried out experimentally. Atomic hydrogen, obtained by passing a powerful electric discharge through molecular hydrogen, when passed into chlorine which has not been illuminated, gives measurable quantities of hydrogen chloride. The amount of hydrogen chloride formed, however, varies with the pressure. Unfortunately, no detectable amount of hydrogen chloride appears to be formed

[1] It has been stated recently that drying has no inhibiting effect on this reaction, and hence one of the difficulties of the Nernst chain theory is removed. See *Annual Reports*, 1933, p. 49.

when illuminated chlorine, which might quite possibly contain chlorine atoms, is passed into ordinary hydrogen. However, hydrogen chloride is produced when chlorine atoms are formed, by chemical reaction, in the presence of hydrogen.

The Nernst chain does not explain the effect of water vapour on the course of the reaction, and Coehn has put forward a theory to take this effect into account. No chain is supposed to occur in the ultra-violet reaction. It is impossible here to enter into a study of the various mechanisms proposed. Enough has been said to show that the problem is one of extraordinary difficulty.[1]

It is interesting to note that heavy hydrogen, H^2, reacts three times as slowly with chlorine as the lighter isotope, H^1, in this photochemical action. If the reaction is carried out with ordinary hydrogen (*i.e.*, a mixture of H^2_2 and H^1_1), the proportion of the heavy isotope increases during the course of the reaction owing to the more rapid removal of the light isotope. The difference in rate occurs in the first part of the chain ($Cl + H^2_2 = H^2Cl + H^2$), there being no difference in the rate in the second part.

Other reactions in which there is great deviation from the law of the photochemical equivalent are the combination of carbon monoxide and chlorine, and the chlorination of methane. In both these cases it is not possible to assume a mechanism like the Nernst chain as, of course, neither CO nor CH_4 can exist in an "atomic" form.

371. Causes of Deviations from the Einstein Law.—Several reasons have been put forward from time to time for the failure of a reaction to obey the Einstein Law of the Photochemical Equivalent. The two main reasons for low quantum yields may be stated as (1) all the absorbing molecules do not react, as before they have a chance to do so, some process involving deactivation occurs, and (2) all the absorbing molecules do not receive enough energy to enable them to react.

Considering the first reason, there may be present in the gas some inert molecules, say, for example, the walls of the vessel, or some impurity, which, on collision with the activated molecule, shares some of its energy, thus making the activated molecule itself not energetic enough to cause reaction. Again, there may be molecules in the substance with which the activated molecules are to combine, which have much less energy than the average, and the absorption of the energy of activation from the active molecule is not enough to bring it to the point of decomposition.

[1] For a detailed account of the hydrogen-chlorine reaction see Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems" (Longmans, 1929), pp. 512–572.

Considering the second reason, it is quite possible that even after the absorption of one quantum of energy by each molecule they may yet be unable to react, being still without sufficient energy. It must be supposed that activation is the movement of an electron in the atom to a level of higher energy (§ 363). When this energy level is high enough, combination will take place. Only those molecules or atoms with electrons already in some level above the normal may be brought into a reactive state by the absorption of one quantum of radiation. This would easily account for low quantum yields.

For reactions with high quantum yields it is necessary to postulate some form of chain reaction, such as in the hydrogen-chlorine reaction (§ 370).

372. The Photochemical Action of X-rays.—Strictly speaking, we should include in the subject of photochemistry the photochemical effects of *X*-rays. The matter is here, however, considerably complicated by the fact that when *X*-rays strike any body they give rise to secondary radiations which are themselves photochemically active. The commonest reaction in which *X*-rays are involved is the photochemical reduction of the silver halides in the photography of *X*-ray pictures. Many other reactions have also been investigated, and the use of *X*-rays in medicine (radio-therapy) is based on the biochemical reactions induced by them.

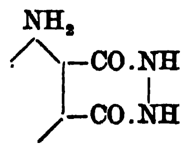
373. The Effect of Sound Waves on Chemical Reactions.—Richards and Loomis (*J. Amer. Chem. Soc.*, 1927, **49**, 3,086) have recently shown that chemical reaction may be accelerated by sound waves of very high frequency (considerably above the highest audible frequency). This radiation is called supersonic radiation. Sound waves, unlike light waves, are made up of a series of rarefactions and compressions in a material medium. When these waves fall on a molecule the effect will be similar to an increase in temperature. Sound waves are capable of causing the detonation of explosives. This would be expected. There are, however, a number of unexpected reactions, *e.g.*, it is said that the rate of hydrolysis of dimethyl sulphate, $(CH_3)_2SO_4$, is accelerated by sound waves of very high frequency.

Supersonic waves can also cause depolymerisation of highly polymerised substances (such as starch $(C_6H_{10}O_5)_n$, which gives dextrin). The fact that depolymerisation has taken place can be shown by viscosity determinations. The hydrolytic decomposition of sucrose into glucose and fructose is also said to occur in traces when a solution of sucrose is placed in a beam of supersonic waves. Paraformaldehyde, hexamethylenetetramine, gum arabic, and gelatin have also been slightly decomposed by this type of wave-motion.

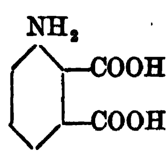
374. Chemiluminescence.—Occasionally when chemical reactions take place, light is emitted. An example of this is the oxidation of phosphorus. This is the reverse process to a photochemical reaction. The light is given out instead of being absorbed. Trautz has collected a list of a number of these changes.

In certain biological reactions light is emitted. The glow of the glow-worm is a case in point.

Of reactions which can be carried out in the laboratory, the most spectacular is the oxidation in alkaline solution of *ortho*-aminophthalic cyclic hydrazide. This substance is a pale yellow crystalline powder, and has the formula



When the hydrazide is dissolved in caustic soda and a little hydrogen peroxide is added, and the liquid dropped from a dropping funnel into an alkaline solution of potassium ferricyanide, as each drop enters the ferricyanide a bright greenish glow is produced. If sodium hypochlorite is substituted for the potassium ferricyanide, the glow is bluish. The chemical changes are complex, but the final product is *ortho*-aminophthalic acid,



Another reaction in which a more feeble glow is emitted is the precipitation of strontium sulphate. A solution of strontium chloride is made, and dilute sulphuric acid is added to it in a dark room.

The most highly luminescent reaction that has yet been observed is the oxidation of the unsaturated silicon compound, silical hydroxide, $Si_2O_2H_2$, by means of permanganate. This was investigated by Kautsky in 1925, who states that the surface luminosity is equivalent to that of a white surface illuminated at a distance of 1·5 metres by a 32 candle-power lamp. In any case, however, the amount of energy liberated in the form of light is very small when regard is had to the amount of substance used.

The light emission from the fire-fly appears to be the most efficient, as judged by eye, because it has a maximum intensity at a wavelength of 5700 Å., at which the eye is most sensitive.

SUMMARY

When light is incident upon a body, part of it is reflected, part may be transmitted and part absorbed. Only that part of the light which is absorbed is effective in bringing about chemical action (Grotthus-Draper Law).

Laws of Absorption of Light.—(*a*) Lambert's law : Equal proportions of the penetrating radiation are absorbed by layers of equal thickness of a homogeneous absorbing medium.

(*b*) Beer's Law : The degree of absorption of light depends upon the thickness of layer traversed and on the molecular concentration in that layer.

Consequences of the Absorption of Light.—I. The primary effect in all cases (except where thermal energy alone is affected) is the electronic excitation of the atom, *i.e.*, the elevation of electrons from levels of low to levels of higher energy. If an electron is completely removed from an atom, the atom is ionised, and this effect is known as the photo-electric effect.

II. Secondary effects : (*a*) The electron reverts instantaneously to its normal state by steps (fluorescence).

(*b*) It reverts to its normal state after a considerable time lag (phosphorescence).

(*c*) It reverts to its normal state after using the energy for chemical reaction (photochemical action).

The energetics of photochemical action are governed by the Einstein *Law of the Photochemical Equivalent*, which states that each molecule entering into reaction has to be excited by the absorption of one quantum of energy. This is probably true of the primary change underlying all photochemical change, *viz.*, the production of the excited atom. There are, however, numerous secondary reactions which completely mask the above Law. The chief types of photochemical change are :—

Type.	*Illustrated by*
1. Dissociation. $XY^* \rightarrow X + Y$.	$2HBr = H_2 + Br_2$. $AgBr = Ag + Br$.
2. Double decomposition. $XY^* + Z \rightarrow XZ + Y$.	$C_6H_{12} + Br_2 = C_6H_{11}Br + HBr$. $CH_2Cl.COOH + H_2O = CH_2OH.COOH + HCl$.
3. Isomeric change. $XY^* \rightarrow YX$.	Maleic acid $\rightarrow$ fumaric acid.
4. (*a*) Addition. $XY^* + Z \rightarrow XYZ$.	$CO + Cl_2 = COCl_2$.
(*b*) Polymerisation. $XY^* + XY \rightarrow X_2Y_2$.	$2C_{14}H_{10} = C_{28}H_{20}$.
(*c*) Chain reactions.	$H_2 + Cl_2 = 2HCl$.
5. Photo-sensitisation. $XY^* + Z = XY + Z^*$. Z* can undergo change as 1–4.	The photo-synthesis of carbohydrates in plants (sensitiser, chlorophyll). The sensitisation of photographic plates (sensitiser, cyanine dyes).

An asterisk denotes that the molecule is excited.

SUGGESTIONS FOR FURTHER READING

GRIFFITH, R., O. and MCKEOWN, A. "Photoprocesses in Gaseous and Liquid Systems." (*Longmans*, 1929.)
KISTIAKOWSKY, G.B. "Photochemical Processes." (*Chemical Catalog Co.*, 1928.)
BALY, E. C. C. "Spectroscopy." Vols. I.–III. (*Longmans*, 1924–1927.)

QUESTIONS

(1) What laws concern the absorption and reflection of light? Discuss their accuracy.

(2) Indicate briefly how a study of absorption spectra can furnish information concerning the structure of compounds.

(3) Describe any one photochemical system with which you are acquainted.

(4) Write an essay on the application of the quantum theory to photochemical processes.

(5) Write notes on fluorescence, phosphorescence, and chemiluminescence, giving some account of their explanation.

(6) How do you account for the fact that in the combination of hydrogen and chlorine by exposure to ultra-violet light more than 10^5 molecules are formed per quantum of energy absorbed?

Does this reaction contravene the law of conservation of energy?

CHAPTER XX

THE STRUCTURE OF MOLECULES

375. The Nature of the Problem.—There are two factors about a molecule that are required when we set out to find the structure of the molecule. They are (1) the actual size of the molecule, *i.e.*, the distances apart of its constituent atoms, and (2) the arrangement of these atoms in the molecule. A good deal of information is now available concerning these questions, at any rate, for the simpler molecules.

When we speak of the distance between two atoms in the molecule, we are apt to convey the idea that the atom is a solid ball, as was postulated by Dalton. It is now known, of course, that atoms are assemblages of electrons, protons, and neutrons, or, according to the more modern views, an assemblage of waves (§ 56). How, then, can we speak of the distance between two atoms when the "size" of the atom cannot be defined? It is usual to take the length of a link as the distance between the nuclei of the two linked atoms. We shall then deal not with the true radius of the atom, but with its "effective" radius, the fraction of the length of the link appropriated by each atom.

A. SPECTROSCOPIC METHODS

376. Molecular Spectra.—Information regarding the lengths of linkages may be obtained from a study of spectra.

The general nature of spectra has already been outlined (§ 45). Line spectra are due to energy transitions in atoms, and are comparatively simple. They have been considered already (Chapter III.). An atom cannot emit a band spectrum; this type of spectrum is entirely characteristic of molecules.

A spectrum band consists of a large number of lines which crowd together towards the "head" of the band. There are usually several groups of these bands in a typical band spectrum. The analysis of such a spectrum is a matter of some complexity, and at present it is only possible to calculate structures with any degree of certainty from the spectra of gases or vapours.

The excitation of the molecular spectrum is a rather more complicated matter than would appear at first sight. The very pro-

duction of the spectrum by passing a discharge through the substance results in the disintegration of the molecule. Consequently, many of the spectra examined have been those of molecules which can have no separate and continued existence in the laboratory, such as HO, NH and CH, but which have been formed by disintegration of some more complex molecule.

In an atom, the absorption of energy can only result in the transition of an electron from an orbit of low energy to one of higher energy. The reverse of this process gives rise to a line in the emission spectrum. In a molecule, there are two further types of energy change: (1) changes in the energy of rotation of the molecule as a whole, and (2) changes in the energy of vibration of the constituent atomic nuclei relative to one another. All three energy changes are quantised. In general, a line in a band spectrum will be conditioned by all three types, the frequency of the line being determined by the algebraic sum of the three energy changes, but spectra due to molecular transitions of rotational energy alone, or of rotational and vibrational energy without electronic transition, are capable of existence, and have been observed.

Considering the rotation spectrum alone, it is to be noted that owing to the quantisation of rotation, the rotation cannot be increased by any arbitrary amount. If the system is rotating, and not emitting, the angular momentum must be a multiple of $h/2\pi$, where h is Planck's constant. For a rigid diatomic molecule it can be shown mathematically that the frequency, ν, of the lines of the spectrum due to purely rotational transitions is given by

$$\nu = \frac{mh}{4\pi^2 I}$$

where m is an integer and I is the moment of inertia of the molecule. For a diatomic molecule,

$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot d^2$$

where m_1 and m_2 are the masses of the atoms and d the distance between them. Clearly, if I can be obtained from observations of the rotation spectrum, d can be found, since m_1 and m_2 are known.

Unfortunately, the pure rotation spectrum lies in the far infra-red, and investigations in this spectral range are difficult. The advent of infra-red photography, however, seems likely to revolutionise this field of investigation. Among the most important of the results obtained are the determinations of the distances between the atoms in the hydrogen halides (Czerny, 1923–27). It is clear that since the moment of inertia, I, involves the masses of the molecules, compounds formed between one element, and various isotopes of

another should have slightly different spectral frequencies. Thus there are two chlorine isotopes of mass 35 and 37 respectively; these will form with hydrogen of mass 1, H^1Cl^{35} and H^1Cl^{37}; and with hydrogen of mass 2, H^2Cl^{35} and H^2Cl^{37}. All these hydrogen chlorides should give rotation spectra slightly displaced from each other, owing to the different masses of the constituent elements. Such isotopic displacements have been observed, not only in the rotation spectra, but also in the rotation-vibration spectra, in which the factor I again appears.

The rotation-vibration spectrum is more easily studied, because it lies mainly in the near infra-red, *i.e.*, the part of the infra-red nearest the visible. If a molecule is regarded as a simple harmonic oscillator, its energy is restricted by quantum considerations to integral multiples of an energy unit, say $h\nu_0$. A pure vibration spectrum is not found, but there are superimposed upon it frequencies due to changes of rotation energy. In deriving the frequency of a line, the algebraic sum of the energies must be used. If the frequency of the lines is represented by ν, then

$h\nu$ = Energy change due to vibrational changes $\pm$ energy change due to rotational changes.

$$= \Delta E_{vib.} \pm \frac{mh^2}{4\pi^2 I}$$

$$\text{or } \nu = \frac{\Delta E}{h}_{vib.} \pm \frac{mh.}{4\pi^2 I}$$

where $\Delta E_{vib.}$ is the change of vibrational energy and m is an integer.

The matter is not, however, quite so simple as this, since, if the vibrational or rotational energy changes, the mean distance between the atomic centres may change, and so must the moment of inertia, I.

Rotation-vibration spectra of polyatomic molecules are very complex. Diatomic molecules with unharmonic binding give bands corresponding to vibrational transitions from $n = 0$ to $n = 1, 2, 3,$ etc., n being the vibrational quantum number. Each band has a fine structure due to rotation. From observations of this fine structure, values of I can be deduced for the non-vibrating molecule and also for the vibrating molecule. From I, the nuclear separation can, of course, be obtained; r increases, as would be expected, as the vibrational energy increases (*i.e.*, as n increases).

If a molecule is more complex than diatomic, it will possess more than one moment of inertia, and by observing the fine structure of the rotation-vibration spectrum the values of these moments can be deduced. A linear molecule can be readily differentiated from a triangular one by observing the different moments of inertia. It is also possible to calculate the angles between the bonds.

If electronic changes occur in the molecule, the energy changes due to these must be superimposed upon the vibrational and rotational energy. This makes the spectrum very complex indeed, especially when it is remembered that the moment of inertia of the molecule will be seriously affected by changes in electronic structure.

377. Raman Spectra—If a beam of monochromatic light is passed through a transparent substance, some of the light is scattered by the molecules in the medium. If this scattered light is examined by means of a spectrometer, it is found that the spectrum is made up of the lines of the original radiation together with a series of lines on either side of them. When the separations of these lines from the line of unchanged frequency are measured, it is found that they correspond to frequencies lying in the infra-red and represent changes in the energy of rotation or vibration. The explanation is that some of the light, on being scattered by the molecules of the medium, picks up or loses one or more quanta of the vibrational or rotational levels. It is thus possible (as it were) to bring the infra-red spectrum into the visible. This phenomenon was predicted by A. Smekal (1923), and was first observed by Sir C. V. Raman (1928).

A great deal of experimental work has been done on the Raman spectra of molecules, which has given valuable information concerning structure. At present, detailed results can only be claimed for the simpler types of molecules. As a result of spectroscopic observations it is known that H_2O, H_2S, ClO_2 and SO_2 are triangular, NH_3 is pyramidal, and $COCl_2$, S_2Cl_2, $SOCl_2$ and CH_2O are probably Y-shaped.

B. X-RAY AND ELECTRON BEAM METHODS

378. Application of X-ray Methods.—It has already been shown how X-ray interference methods enable the structure of crystals to be deduced. Debye (1929) found that gases and vapours, and also liquids, gave X-ray interference patterns when a technique similar to the powder technique (§ 126) is used. A beam of X-rays, limited by slits, is passed through a vessel through which the gas is flowing, and the interference pattern is obtained on a photographic plate. In the case of a liquid, the results are difficult to interpret, as it is not known whether the scattering is due to atoms in the same molecule or in neighbouring molecules. In a gas, however, the separation between the molecules is much greater than the nuclear separation of the atoms in the individual molecules, and the method can, therefore, be used to find this nuclear separation. It is known that the scattering is not due to the nuclei themselves, but to the orbital electrons, so the distances measured are not the same as

those obtained by infra-red spectroscopy. The "centre" of the atom indicated by X-ray interference is the mean centre of the electronic orbits and not the nucleus.

379. Electron-ray Interference Method.—In dealing with the structure of crystals, it was mentioned that a beam of electrons could be substituted for X-rays in obtaining the interference patterns. This method has been applied to gases and vapours by Wierl (1930), the results agreeing very well with those obtained by the X-ray method, though probably the latter is the more accurate. The Wierl method has numerous advantages over the X-ray method as regards technique. Since the number of scattering particles is much less in a gas than in a solid, the exposures required in the X-ray method are very long. When first used by Debye, the method required an exposure of twenty-four hours, though this has now been reduced to four to five hours. The electron beam is considerably more intense than the X-ray beam (electrons of 40 kw. energy were used by Wierl), so that the exposure in Wierl's method need only be one-fifth of a second. Also, it would be impossible to use the X-ray method under reduced pressure, as the number of particles would be even smaller than under atmospheric pressure, and the exposure correspondingly longer. The vapours of liquids which boil under atmospheric pressure with decomposition could not therefore be investigated by the X-ray method, whereas results could be obtained by the electron-beam method at reduced pressure.

C. DIPOLE MOMENTS OF MOLECULES

380. The Dielectric Constant.—A study of the dielectric constants of substances has recently given us a great deal of insight into the structure of molecules. It also helps us to understand the process of ionisation, and there is no doubt that it is one of the most important constants characterising matter.

It may be necessary to explain what the dielectric constant is.

If we have two electric charges, e, separated by a distance r in a vacuum, then the force between them will be given by

$$F = e^2/r^2.$$

This force will be one of repulsion if the two charges are of the same sign, and one of attraction if they are opposite in sign.

This law holds only in a vacuum. If we study the force between two charges in any other medium, say air or water, then

$$F = e^2/\epsilon r^2$$

where ϵ is a constant pertaining to the medium, called the *dielectric constant*.

The dielectric constant for air is nearly 1, and so the law of force between point charges is almost the same in air as in a vacuum. In many media, however, the dielectric constant is considerable, and the force is correspondingly reduced. The values of some

TABLE CXVIII.—DIELECTRIC CONSTANTS

Substance.	ϵ
Plate glass	4·67
Ebonite	3·15
Sulphur	3·84
Mica	6·64
Paraffin wax	2·3
Petroleum	2·0
Water	81·7
Ethyl alcohol	25·4
Air (76 cm. pressure)	1·0006

dielectric constants are given in Table CXVIII. The data for some liquids are also to be found in Table LII, p. 55.

A system composed of two charged parallel plates is called a "condenser," and has a certain capacity in a vacuum, given by the equation

$$C = Q/V$$

where C is the capacity, Q is the charge and V the potential. If the medium between the plates has a dielectric constant ϵ, then the capacity is given by

$$C = \epsilon Q/V.$$

This provides a useful method of determining the dielectric constant of any medium.

It was discovered by Clerk-Maxwell, in his work on the electromagnetic theory of light, that the dielectric constant of a medium, as determined by the above static method, is intimately connected with its refractive index for radiation of infinite wavelength. The dielectric constant is given in fact by the square of the refractive index, under these conditions, and this has been proved experimentally for many substances.

381. Methods of Determining Dielectric Constants.—This can be but a brief outline. For a more complete account a text-book of physics should be consulted.

The chief methods fall into three classes :—

(1) The measurement of the electric force acting through a dielectric.

(2) The determination of the velocity of propagation of electromagnetic waves through a material. This is inversely proportional to the square root of the dielectric constant of the substance. The method merely involves the measurement of the refractive index of the substance (§ 380).

(3) The measurement of the capacity of a condenser when there is nothing between the plates, and when the latter are separated by a dielectric. The most important methods fall into this class.

In modern times dielectric constants are nearly always determined by finding the capacity of a condenser by an oscillatory circuit method. It is well known that the frequency of oscillation of a circuit depends upon its capacity, its inductance, and its resistance. The frequency of oscillation is fairly easily determined, whence it follows that if the inductance and resistance are kept constant the capacity can be determined by comparison with a standard condenser.

382. Dipole Moments.—Molecules consist of an assemblage of protons and electrons (or possibly neutrons, positrons and electrons). As a rule, the centre of action of the positive parts will not coincide with that of the negative parts of the molecule, and so the molecule may be imagined to consist of a system which reduces to two point charges of equal and opposite sign, separated by a rigid link or rod.

The two charges must of course be equal, otherwise there would be a resultant charge on the molecule. The electrical dipole moment of such a system as that just described is defined as ed, where e is the charge on each end of the rod and d is the length of the rod. This quantity is usually referred to merely as the *dipole moment* of the molecule.

It is clear at once that a knowledge of the dipole moment will tell us a good deal about the constitution of the molecule. Consider a compound formed from two atoms. The atoms themselves before combination are neutral. They have no dipole moment, since every isolated atom must have the centre of action of its positive portion, *i.e.*, the nucleus, at the centre of action of the surrounding electrons. When combination occurs we may suppose that the two atoms become bound by a co-valent link. According to Sidgwick, this means the sharing of two electrons between the orbits of the two atoms. According to Sugden, singlet linkages are possible; but it does not matter which theory we take for our present purpose. If the bonding electrons are shared equally between the two atoms the resulting molecule will be non-polar, and will possess no dipole moment, for the effective arrangement

of the positive and negative portions has not been altered; but suppose that one atom takes a greater share of the two electrons than the other, then the molecule becomes polar, because one atom will have a preponderance of negative electricity associated with it, and the other must, in consequence, have a deficit of negative charge. If then a substance possesses a dipole moment, this indicates that the sharing of the electrons has not been equal.

383. Determination of Dipole Moments.—Let us consider what happens when a gas or vapour is placed in an electric field. First of all, the molecules will, if they possess a dipole moment, tend to set themselves in a direction so that their fields act in opposition to the electric field. The same behaviour is seen exactly with a set of compass needles placed in a magnetic field. They all tend to turn in one direction, so that their north poles point to the south pole of the field. This tendency, however, on the part of the molecules will be opposed by the thermal agitation of the molecules which makes for random orientation, and also by the effect of the neighbouring molecules on one another. Thus, when the substance is placed in an electric field, it is not to be expected that complete orientation in one direction will be achieved. The extent of it will depend upon the strength of the field, and upon the physical environment of the molecules. This effect is called the *orientation polarisation*. Another effect is to be noted. Whether the molecules possess a dipole moment or not, the electrons will be displaced slightly from their normal orbits and attracted towards the positive pole of the field. This is called the *electron polarisation*. In addition, the nuclei themselves will be slightly displaced relative to each other. This is called the *atomic polarisation*, and is usually small.

We may sum up what we have been saying by noting the existence of the three types of polarisation :—

(1) *Orientation polarisation*, P_o.
(2) *Electron polarisation*, P_e.
(3) *Atomic polarisation*, P_a.

The electron and atomic polarisation together make up the polarisation due to distortion of the molecule, and we may write for their sum, P_d. Hence, the total polarisation

$$P = P_d + P_o = P_e + P_a + P_o.$$

It was shown by Debye that the "Clausius-Mosotti" relationship, which states that the polarisation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

where M is the molecular weight, d the density and ϵ the dielectric constant, measured the total molecular polarisation of the substance. The dielectric constant of the medium will obviously depend on the total effect of the molecules on the field, and this fact finds expression in the above equation.

It may be compared with the Lorentz-Lorenz refraction equation (§ 113)

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n is the index of refraction and R is the molecular refractive power. It is clear from what we have said about the effect of thermal agitation on the orientation that the polarisation should vary with temperature ; yet no allowance was made for this in the derivation of the above equation. Also, it has been stated that the dipoles will have some influence on each other, and this will clearly depend on their proximity, and therefore on the molecular concentration ; yet again there was no allowance for this in deriving the formula.

It is obvious from the above that, in order to measure the permanent dipole moment of the molecule, we must eliminate the electron and atomic polarisations. If the molecular polarisations of a substance in the vapour and solid state are compared, the approximate value of the orientation polarisation, P_o, can be obtained, since in the solid state there is little or no possibility of orientation, the molecules being firmly held in the crystal lattice. The polarisation in the solid state is due to $P_a + P_e$ alone. P_o can be obtained from the total polarisation P measured for the vapour, by subtracting $P_a + P_e$ obtained for the solid.

When a molecule is exposed to an alternating electromagnetic field instead of to a steady one, if the alternations are very rapid the molecules will not have time to orient themselves, and so the polarisation will be dependent only upon the distortion effect. Ordinary light can be used for the rapidly alternating field, the quantity measured being the refractive index instead of the dielectric constant. The alternations in the visible are too rapid for the heavy nuclei to be displaced and so, if the total distortion polarisation is to be measured, it is necessary to use infra-red light. This then provides a method for distinguishing between P_a and P_e. P_a is found by determining the total polarisation due to distortion using infra-red rays, and then subtracting P_e found for visible rays.

Since the orientation depends on an equilibrium between complete orientation and the effect of thermal agitation, it follows that the orientation will decrease as the temperature is increased and thermal agitation becomes more violent. The exact relation between

temperature and the molecular orientation polarisation, P_o, was deduced by Debye in the following form :—

$$P_o = \frac{4\pi}{3} \cdot N \frac{\mu^2}{3kT},$$

where μ is the dipole moment in electrostatic units, N is Avogadro's number, k is Boltzmann's constant (§ 268) and T the absolute temperature. The total polarisation will be

$$P = P_a + \frac{4\pi N\mu^2}{9kT}$$

$$A + \frac{B}{T},$$

where $$B = \frac{4\pi N\mu^2}{9k}.$$

If the molecular polarisation is plotted against the reciprocal of the temperature we shall get in all cases a straight line if the above equation is satisfied ; but, if the substance is non-polar, then $B = 0$, since $\mu = 0$, and the straight line is horizontal. If the substance is polar, B has a definite value, and the line has a slope from which B can be calculated. Putting the numerical values of N ($6{\cdot}06 \times 10^{23}$) and k ($1{\cdot}37 \times 10^{-16}$) in the above equation, we have

$$\mu = 0{\cdot}0127\sqrt{B} \times 10^{-18} \text{ electrostatic units},$$

so that μ can be easily obtained from B.

The Clausius-Mosotti relationship (p. 740) states that

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}.$$

Hence, combining this with Debye's equation,

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = A + \frac{B}{T}.$$

For the majority of vapours ϵ is very nearly equal to 1. Thus, for water, at 120° C., ϵ is 1·004002 e.s.u. Consequently, $(\epsilon + 2)$ is approximately equal to 3. Hence $(\epsilon - 1)$ should vary linearly with $\frac{1}{T}$, since $(\epsilon + 2)$, M, and d, as well as A and B, are constant. This, of course, is only approximately true, since $(\epsilon + 2)$ is not quite constant.

The following Table (CXIX.) contains data for water, methyl and ethyl ethers, and methyl chloride, taken from a paper by R. Sänger on " New measurements on the effect of temperature on the dielectric constants of gases and vapours " (1929).[1]

These figures are plotted in Fig. 209, which shows the graphs between $10^3/T$ and $(\epsilon - 1) \times 10^5$. The linear nature of the curves

[1] This paper is the first in the series of the " Leipzig Vorträger " on " Dipole Moment and Chemical Structure." This series has been translated into English by W. M. Deans (Blackie), under the above title.

TABLE CXIX.—VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE

Water.			Methyl ether.			Ethyl ether.			Methyl chloride.		
$T°$ Abs.	$10^3/T$	$(\epsilon - 1) \times 10^6$	$T°$ Abs.	$10^3/T$	$(\epsilon - 1) \times 10^6$	$T°$ Abs.	$10^3/T$	$(\epsilon - 1) \times 10^6$	$T°$ Abs.	$10^3/T$	$(\epsilon - 1) \times 10^6$
393·0	2·545	400·2	298·0	3·356	465·5	313·0	3·195	495·0	298·0	3·356	797·6
423·0	2·364	371·7	338·0	2·959	426·7	353·0	2·833	470·0	338·0	2·959	718·3
453·0	2·207	348·8	378·0	2·646	398·1	393·0	2·545	450·7	378·0	2·646	657·8
483·0	2·070	328·7	418·0	2·392	372·2	433·0	2·310	431·0	418·0	2·392	607·2

is in complete agreement with Debye's theory. The curves for carbon tetrachloride and methane are also given in Fig. 209. Both these substances are non-polar, and therefore give a straight line parallel to the temperature axis.

The values obtained for the dipole moments, calculated from the slopes of the curves, are :—

Methyl chloride	$(1{\cdot}86 \pm 0{\cdot}03) \times 10^{-18}$ e.s.u.
Ethyl ether	$(1{\cdot}10 \pm 0{\cdot}02) \times 10^{-18}$ e.s.u.
Water	$(1{\cdot}84_7 \pm 0{\cdot}02) \times 10^{-18}$ e.s.u.
Methyl ether	$(1{\cdot}32 \pm 0{\cdot}02) \times 10^{-18}$ e.s.u.
Carbon tetrachloride	0
Methane	0

This is the most accurate method of determining dipole moments, but unfortunately the range of temperature required for accurate results is large, and it can therefore only be applied to those substances which do not undergo decomposition within the temperature range used.

There is another method for measuring dipole moments which does not depend upon the dielectric constant at all, but upon direct measurement of the behaviour of molecules in an electric field It is called the "molecular beam method,"[1] and is based on a method first mentioned by Kallmann and Reiche, and later used by Stern and Gerlach for the determination of the magnetic moment of atoms. The substance is obtained in such a state that the molecules are far apart from one another, and move along without collision, by heating it in a small oven, and a beam of such molecules is obtained by allowing them to pass through a very narrow slit into a high vacuum, the beam being further defined by another slit. This

[1] For a full account of the use of the molecular beam method, the student is recommended to see Estermann's paper in "Dipole Moment and Chemical Structure," trans, W. M. Deans (Blackie).

beam is passed through an intense non-uniform electric field when, if the dimensions of the beam and the intensity and inhomogeneity of the field remain fixed, the beam is deviated through an angle dependent upon the electric moments of the molecules. The molecular beam is allowed to impinge on a receiver cooled in liquid air, to which the molecules adhere and leave behind a trace of the solid material, which can be viewed through a microscope. All molecules, irrespective of whether they bear a dipole moment or not, will have one induced in them by the field, but this will only cause a deviation parallel to the direction of the field. The presence of a polar molecule is indicated by a broadening of the trace, and,

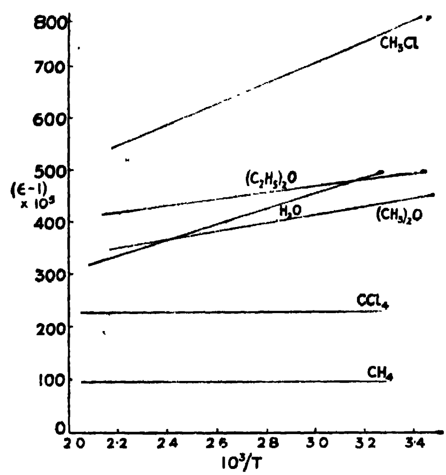


FIG. 209.—$P - \frac{1}{T}$ Curves for Various Compounds.

by a complicated calculation, the two effects can be separated and the dipole moment calculated.

This method has proved useful in the case of substances which are not soluble in non-polar solvents (a condition required for the determination of the dielectric constants of substances at radio frequencies employed in the first method described), or else do not give sufficient vapour to enable the dielectric constants to be measured by the second method. The only condition required is that the substance should be capable of being obtained as a molecular beam. It has been used for the determination of the moments of alkali metal halides, and a notable example is its application to penterythritol.

According to a theory put forward by Weissenberg, a carbon

compound of the type CA_4 should be able to exist in two forms, one a regular tetrahedron, with the carbon atom in the centre, and the four A groups at the apices, and the other a pyramid with the carbon atom at the vertex and the A groups at the base. Obviously, a molecule of the first type should possess no dipole moment, whilst one with the pyramidal structure should possess a permanent moment. Penterythritol, $C(CH_2OH)_4$, cannot be examined by the dielectric constant method, being insoluble in non-polar solvents, and decomposing when vaporised under all but very low pressures. Examination of this substance by the molecular beam method, however, shows that its dipole moment is about 2×10^{-18} e.s.u. (Estermann, 1929). Penterythritol acetate also has a moment, but the bromide is non-polar. Estermann states that the observations do not necessarily prove the accuracy of the assumption of a pyramidal model for molecules of the type CA_4, but do at least show that penterythritol as a whole shows no central symmetry, of which tetrahedral symmetry is one type.

It should be remembered that in all methods of determining the dipole moments of molecules the substance under investigation must either be in the gas or vapour state, or else must be in very dilute solution in a non-polar solvent. This stipulation is necessary in order to eliminate interaction between the molecules themselves. In the usual case in which the substance is investigated in a non-polar solvent, it is necessary to extrapolate to infinite dilution.

384. Results of Dipole Moment Determinations.—It is well to point out exactly what is determined in these experiments. The value obtained is the resultant moment for the whole molecule, and where this is complex, all the links will have contributed to it. The results merely indicate the product *ed*, where *e* is the resultant charge at the end of the dipole which has the equivalent length *d*.

Consider a diatomic molecule, A—B. If an electron were transferred completely from A to B, the dipole moment would be $4{\cdot}77 \times 10^{-10} . d$, where d is the distance between the nuclei and $4{\cdot}77 \times 10^{-10}$ is the charge associated with the electron. The distance between the nuclei will be approximately the molecular diameter, which is about 10^{-8} cms. Hence, the dipole moment of a molecule existing in the ionic state should be in the neighbourhood of $4{\cdot}77 \times 10^{-18}$ e.s.u.

The dipole moments of most polar substances are less than this, but in a few cases, higher values have been found. Thus, the dipole moments of potassium iodide, potassium chloride and sodium iodide, determined by the molecular beam method are $6{\cdot}8 \times 10^{-18}$, $6{\cdot}3 \times 10^{-18}$ and $4{\cdot}9 \times 10^{-18}$ e.s.u., respectively (Scheffers, 1934). These high values are probably due to deformation of the orbits of

the valency electrons. It is clear that the dipole moment gives some idea of the degree of sharing of electrons between the atoms linked. For equal sharing, the moment would be zero.

TABLE CXX.—DIPOLE MOMENTS

Throughout this chapter the factor 10^{-18} will be omitted. Thus, when the dipole moment of water is given as 1·85, this stands for $1{\cdot}85 \times 10^{-18}$ e.s.u.

Substance.	Formula	Moment.
Methane	CH_4	0
Ethane	C_2H_6	0
n-Pentane, *iso*-Pentane	C_5H_{12}	0
Ethylene	$CH_2=CH_2$	0
Acetylene	$CH\equiv CH$	0
Methyl alcohol	CH_3OH	1·78
Ethyl alcohol	C_2H_5OH	1·85
Methyl iodide	CH_3I	1·90
Nitromethane	CH_3NO_2	3·8
Acetonitrile	CH_3CN	3·51
Acetone	$CH_3 . CO . CH_3$	2·72
Benzene	C_6H_6	0
Chlorobenzene	C_6H_5Cl	1·53
Nitrobenzene	$C_6H_5NO_2$	3·8
Diphenyl	$C_6H_5-C_6H_5$	0
Argon, hydrogen, nitrogen	A, H_2, N_2	0
Hydrogen chloride	HCl	1·03
Hydrogen bromide	HBr	0·78
Hydrogen iodide	HI	0·38
Water	H_2O	1·85
Ammonia	NH_3	1·5
Sulphur dioxide	SO_2	1·7
Hydrogen sulphide	H_2S	0·93
Silver perchlorate	$AgClO_4$	4·7

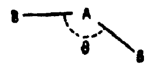
It has been pointed out by J. J. Thomson that as moments are vector quantities they can be added vectorially, *e.g.*, as in the determination of the resultant of two or more forces by the application of the parallelogram of forces. This method has proved very useful in deciding the moments of various linkages.

Monatomic substances must of course be non-polar. The rare gases possess no moment.

Diatomic molecules (with the exception of elements) are all polar so far as they have been determined. With triatomic molecules we have the possibility of either symmetrical or asymmetrical arrangement, and so the moment may be either zero or finite. Thus, if the

molecule is of the type AB_2, and A lies between two B atoms in a straight line, then the substance will be non-polar if the two links are the same.

B—A—B

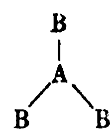


I. II

FIG. 210.—Models of Triatomic Molecules.

If, however, one link makes an angle with the other, as in II. above, the molecule will possess a moment given by $M = 2m \cos \frac{1}{2}\theta$, where m is the moment of a single link and θ the angle between them. Water is polar, and must therefore be constructed in this way. Where there are double links, as in O=C=O, the tetrahedral arrangement of the carbon bonds would mean that this must be a linear molecule, and possess no moment. For this reason CO_2 and CS_2 are not polar.

Tetratomic molecules of the type AB_3 are non-polar if all four atoms lie in one plane, and the angles between the bonds are all equal, as they must be in the case of AB_3.



Where the model is pyramidal, one atom will lie out of the plane of the rest and the molecule will be polar.

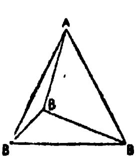


FIG. 211.—Pyramidal Model of AB_3 Molecule.

Hence, the polarity found for ammonia, phosphine, arsine and the trihalides of phosphorus, arsenic and antimony.

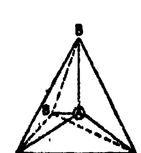


FIG. 212.—Model of AB_4 Molecule.

Pentatomic molecules of the form AB_4 should be non-polar on the tetrahedral model or on the plane model. The pyramidal structure would give a finite value of μ. It is found that methane, carbon tetrachloride, silicon tetrachloride, titanium tetrachloride, etc., are all non-polar. Penterythritol, however, has a definite moment (p. 745).

These simple examples of the application of the dipole moment to the elucidation of molecular structure show the value of the method. In the cases we have quoted there is only one type of link, and, of course, the matter becomes much more complicated when we deal with complex organic molecules in which several types of link occur. By making the assumption that the presence of one link does not influence the rest of the molecule,[1] it is possible, by comparing the moments of molecules in which groups are replaced by others, to find the moments associated with individual links. This has been done in very many cases, and a Table of the results taken by permission from Sidgwick's "Covalent Link in Chemistry" is given below :—

TABLE CXXI.—DIPOLE MOMENTS OF LINKAGES

H—C	0·2	H—N	1·5	H—O	1·6	H—F	(2)
		H—P	0·55	H—S	0·8	H—Cl	1·03
		H—As	0·15			H—Br	0·78
						H—I	0·38
		C—N	0·4	C—O	0·9		
				C=O	2·5		
		C≡N	3·3	C≡O	5·3		
				C—S	1·2	C—Cl	1·7
				C=S	3·0		
				C—Se	1·1	C—Br	1·6
P—Cl	0·8	P—Br	0·6	C—Te	0·9	C—I	1·4
As—Cl	2·0	As—Br	1·7				
Sb—Cl	3·9	N=O	1·9				

Knowing the moments of individual links, it is possible to work out the distribution of residual charges in the molecule owing to the unequal sharing of the electrons in the linkages. In the case of hydrogen chloride with the single H—Cl linkage, the moment of this body is 1·03, whilst the distance between the atoms, determined by other means, is 1·27 Å. The moment is the product of one of the

[1] It is very probable that deformation of the orbits of the valency electrons often occurs in substances containing an electrovalent linkage, *e.g.*, in potassium iodide (p. 745). The remarks concerning the dipole moments of linkages, etc., must be understood to refer to covalent compounds.

residual charges and the distance, and if the residual charge is supposed to reside on the nucleus, then each charge must be $1{\cdot}03/1{\cdot}27 = 0{\cdot}81 \times 10^{-10}$ e.s.u. This can be better expressed as a fraction of the charge on the electron, $4{\cdot}77 \times 10^{-10}$ e.s.u. In this case it is $0{\cdot}81/4{\cdot}77 = 0{\cdot}170$. There will be a charge of $+ 0{\cdot}170$ on the H atom and $- 0{\cdot}170$ on the Cl atom. In this way the residual charges due to various linkages have been calculated, and some of them are given in the Table. The positive atom is written first.

TABLE CXXII.—RESIDUAL CHARGES

(Taken, by permission, from "The Covalent Link in Chemistry," by Professor N. V. Sidgwick.)

Link.	Moment. $\Delta E \times d$. e.s.u.	Distance. d. Å	ΔE. e.s.u.	$\frac{\Delta E}{e} = F$.
H—C	0·2	1·14	0·18	0·04
H—N	1·5	1·08	1·4	0·29
H—O	1·6	1·07	1·5	0·31
H—S	0·8	1·43	0·6	0·13
C—N	0·4	1·48	0·3	0·06
C≡N	3·3	1·15	2·9	0·61
C—O	0·9	1·47	0·6	0·13
C=O	2·5	1·27	2·0	0·42
C—S	1·2	1·83	0·7	0·15
C=S	3·0	1·59	1·9	0·40
C—Cl	1·7	1·74	1·0	0·21
C—Br	1·6	1·90	0·8	0·17
C—I	1·4	2·12	0·7	0·15

In the last column, the ratio of the residual charge ΔE on the nucleus to the charge on the electron, e, is calculated.

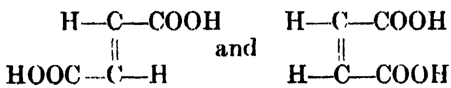
These figures enable us to determine roughly the places in the molecule where there is an excess or deficit of charge. In the determination of the residual charges present in molecules which are more complex, the amount for each link must be added. Consider the case of methyl chloride. Each C—H linkage has a charge of $+ 0{\cdot}04$ on the hydrogen. This would give for the carbon attached to the three hydrogen atoms a charge of $- 0{\cdot}12$. There is another linkage, however, the C—Cl link. This has a charge on the Cl of $- 0{\cdot}21$, and a corresponding charge of $+ 0{\cdot}21$ on the carbon. Hence the total charge on the carbon is $- 0{\cdot}12 + 0{\cdot}21 = + 0{\cdot}09$. Where there is a co-ordinate link in the molecule the value 1·4 must be added or subtracted from the appropriate atom. The co-ordinate link adds 1 to the donor and removes 1 from the acceptor.

The diagrams below (Fig. 213) have been drawn up in this way (mainly from Sidgwick, " The Covalent Link in Chemistry ").

It is obvious that the study of dipole moments can be of great use in deciding questions of *stereoisomerism* in organic chemistry. Thus, in dealing with *cis- trans*-isomerism of ethylene derivatives,

cis trans

e.g., fumaric and maleic acids,



fumaric acid maleic acid

it is clear that the *cis-* form will be polar, whilst the *trans-* form

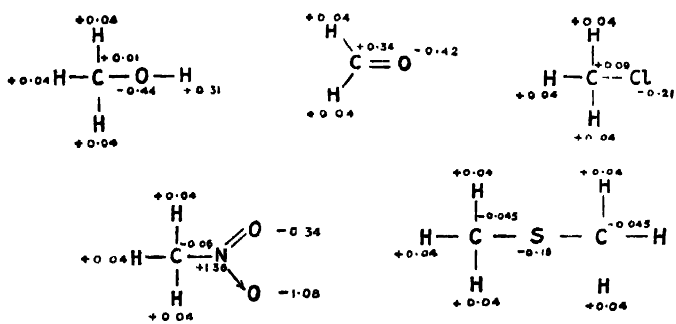
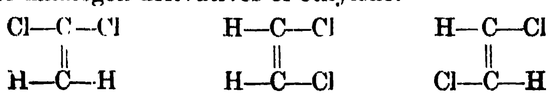


FIG. 213.—Residual Charges on the Atoms of Various Compounds.

will be non-polar. This has been confirmed by experiment in the case of the dihalogen derivatives of ethylene.



asymmetrical dichlorethylene cis trans

symmetrical dichlorethylene

There are three dichloro derivatives of ethylene, the formulæ being shown above. Of these, the first is easily recognised on account of its chemical properties, but the *cis-* and *trans-* forms are not thus recognisable. One of these compounds has been shown to possess a dipole moment of 1·9 e.s.u., and the other zero. The *cis-* form can thus be differentiated from the *trans-* form. This work has been carried out by Errera, who found the following values for the moments of other dihalogen derivatives of ethylene.

Substance.	Moment.
cis-dibromo-ethylene	1·4
trans-dibromo-ethylene	0
cis-diiodo-ethylene	0·8
trans-diiodo-ethylene	0
cis-chlorobromo-ethylene	1·6
trans-chlorobromo-ethylene	0

Much light is thrown on the question of *benzene substitution* by the study of dipole moments. Benzene itself has no dipole moment, and it is concluded from this and other evidence (supplied by the *X*-ray structure of hexamethyl-benzene) that the carbon and hydrogen atoms all lie symmetrically in a plane.

In the theories of benzene substitution and the positions taken up in the ring by various substituents, put forward by organic chemists, a displacement of electrons in the molecule is assumed. If this does happen, it must be shown in the dipole moments. The moment of a group C—X has been shown in general to be different according as the carbon is part of an alkyl group or an aryl group. Sutton has been able to show that there is a relationship between the difference of the moment of (Ar—X) and (Alk—X), and the directing power of the substituent X. If the moments of which the positive end is remote from the alkyl or aryl group are called positive, and the reverse of this negative, then when the moment of (Ar—X)

TABLE CXXIII.—MOMENTS OF AROMATIC AND ALIPHATIC DERIVATIVES

(Data taken, by permission, from "The Covalent Link in Chemistry," by Professor N. V. Sidgwick.)

X.	Moment of the linkage (Ar – X).	Moment of the linkage (Alk – X).	Difference m(Ar – X) – m(Alk – X).	Orientation
CH_3	+ 0·45	± 0·0	+ 0·45	o & p
NH_2	+ 1·55	+ 1·23	+ 0·32	o & p
Cl	– 1·56	– 2·15	+ 0·59	o & p
Br	– 1·52	– 2·21	+ 0·69	o & p
I	– 1·27	– 2·13	+ 0·88	o & p
CH_2Cl	– 1·82	– 2·03	+ 0·21	o & p
$CHCl_2$	– 2·03	– 2·06	+ 0·03	o, p or m
CCl_3	– 2·07	– 1·57	– 0·50	m
$COCH_3$	– 2·97	– 2·79	– 0·18	m
CO	– 3·04	– 2·76	– 0·28	m
C≡N	– 3·89	– 3·46	– 0·43	m
NO_2	– 3·93	– 3·05	– 0·88	m

minus that of (Alk—X) is positive X directs further substitution into the ortho- and para-positions. If the difference is negative it directs further substitution into the meta-position. This behaviour has been explained and is stated to show that there is an electron drift in benzene when mono-substitution takes place, which decides where future substituents will go.

It has also been shown that the results obtained in this way give an explanation of the rule put forward by Hammick and Illingworth for the positions of substituents in the benzene nucleus. This rule, to which there are no exceptions, states that: If, in a substitution product of benzene, C_6H_5—X—Y, Y is in a later group of the periodic table than X, or if, being in the same group, Y is of a lower atomic weight than X, the direction of subsequent substitution is meta. If Y is in an earlier group, or if there is no Y, then the direction is ortho-para. This is very easily explained on the dipole theory, since the position of an element in the periodic table decides the sign of the dipole formed by it with another element.

The theory has also been applied to the naphthalene and diphenyl derivatives with considerable success.

SUMMARY

Information concerning the structure of molecules can be obtained from (*a*) spectroscopic data, (*b*) *X*-ray methods, (*c*) investigation of the dipole moment of a molecule.

Atoms give line spectra, corresponding to electron transitions from levels of high to levels of lower energy. Molecules give band spectra. These are due to variations in the rotational and vibrational energy of the molecule as a whole, this energy being quantised in a similar way to that of the electrons in their orbits. The spectrum due to rotation alone is in the far infra-red. That due to rotation superimposed upon vibration is in the near infra-red. Investigation of these spectra enables the moment of inertia (or moments of inertia) of the molecule to be obtained. From the moment of inertia the nuclear separation of the atoms in the molecule can be calculated. It is also possible to work out the angles between the linkages in a molecule.

When the centre of gravity of the negatively charged parts of the molecule does not coincide with that of the positively charged parts, the molecule is polar. Its electrical field will correspond to that of two equal and opposite charges separated by a fixed distance. The product of the charge and the distance is the dipole moment of the molecule. The value of this enables some molecular structures to be inferred.

It is possible to determine the moment associated with various linkages, and hence to find the distribution of polarity in the molecule. Such results have led to conclusions concerning stereochemistry, benzene substitution, and other problems of organic chemistry.

SUGGESTIONS FOR FURTHER READING

SIDGWICK, N. V. "The Covalent Link in Chemistry." (*Cornell University Press*, 1933.)

SIDGWICK, N. V., and BOWEN, E. J. "The Structure of Simple Molecules" in the "Annual Reports of the Progress of Chemistry," 1931. (*Chemical Society*, 1931.)

DEBYE, P. "Polar Molecules." (*Chemical Catalog Co.*, 1928.)

SMYTHE, C. P. "Dielectric Constant and Molecular Structure." (*Chemical Catalog Co.*)

DEBYE, P. Trans. DEANS. "Dipole Moment and Chemical Structure." (*Blackie*, 1933.)

DEBYE, P. Trans. DEANS. "The Structure of Molecules." (*Blackie*, 1932.)

The student is advised to read some of the original papers. These can be discovered by consulting British Chemical Abstracts A, or the Chemical Abstracts published by the American Chemical Society. The Annual Reports of the Chemical Society are invaluable.

If the student has access to *Nature*, it will be of great help to him to read the articles of chemical interest.

QUESTIONS

(1) Show in what ways a knowledge of the dielectric constant of a substance may throw light on its constitution.

(2) Water has a dipole moment of 1·98. What does this statement mean, and what does it imply?

(3) Describe the various types of spectra emitted by atoms and molecules. Explain the differences between them.

(4) Show how the structure of a simple molecule can be investigated by a study of spectra.

ATOMIC WEIGHTS, 1947

Taken by kind permission from the *Journal of the Chemical Society*, July 1947.

Atomic number	Name	Symbol	Atomic weight	Atomic number	Name	Symbol	Atomic weight
1	Hydrogen .	H	1·0080	47	Silver .	Ag	107·880
2	Helium .	He	4·003	48	Cadmium .	Cd	112·41
3	Lithium .	Li	6·940	49	Indium .	In	114·76
4	Beryllium .	Be	9·02	50	Tin .	Sn	118·70
5	Boron .	B	10·82	51	Antimony .	Sb	121·76
6	Carbon .	C	12·010	52	Tellurium	Te	127·61
7	Nitrogen .	N	14·008	53	Iodine .	I	126·92
8	Oxygen .	O	16·0000	54	Xenon .	Xe	131·3
9	Fluorine .	F	19·00	55	Cæsium .	Cs	132·91
10	Neon .	Ne	20·183	56	Barium .	Ba	137·36
11	Sodium .	Na	22·997	57	Lanthanum .	La	138·92
12	Magnesium .	Mg	24·32	58	Cerium .	Ce	140·13
13	Aluminium .	Al	26·97	59	Praseodymium	Pr	140·92
14	Silicon .	Si	28·06	50	Neodymium	Nd	144·27
15	Phosphorus .	P	30·98	61	Illinium .	Il	—
16	Sulphur .	S	32·066	62	Samarium	Sm	150·43
17	Chlorine .	Cl	35·457	63	Europium .	Eu	152·0
18	Argon .	A	39·944	64	Gadolinium	Gd	157·3
19	Potassium .	K	39·096	65	Terbium .	Tb	159·2
20	Calcium .	Ca	40·08	66	Dysprosium .	Dy	162·46
21	Scandium .	Sc	45·10	67	Holmium .	Ho	163·5
22	Titanium .	Ti	47·90	68	Erbium .	Er	167·64
23	Vanadium .	V	50·95	69	Thulium .	Tm	169·4
24	Chromium .	Cr	52·01	70	Ytterbium .	Yb	173·04
25	Manganese .	Mn	54·93	71	Lutecium .	Lu	175·0
26	Iron .	Fe	55·85	72	Hafnium .	Hf	178·6
27	Cobalt .	Co	58·94	73	Tantalum .	Ta	181·4
28	Nickel .	Ni	58·69	74	Tungsten .	W	184·0
29	Copper .	Cu	63·54	75	Rhenium .	Re	186·31
30	Zinc .	Zn	65·38	76	Osmium .	Os	191·5
31	Gallium .	Ga	69·72	77	Iridium .	Ir	193·1
32	Germanium .	Ge	72·60	78	Platinum .	Pt	195·23
33	Arsenic .	As	74·91	79	Gold .	Au	197·2
34	Selenium .	Se	78·96	80	Mercury .	Hg	200·61
35	Bromine .	Br	79·916	81	Thallium .	Tl	204·39
36	Krypton .	Kr	83·7	82	Lead .	Pb	207·22
37	Rubidium .	Rb	85·48	83	Bismuth .	Bi	209·00
38	Strontium .	Sr	87·63	84	Polonium .	Po	—
39	Yttrium .	Y	88·92	85	—	—	—
40	Zirconium .	Zr	91·22	86	Radon .	Rn	222
41	Niobium .	Nb	92·91		(Emanation) .	(Em)	
	(Columbium) .	(Cb)		87	—	—	—
42	Molybdenum .	Mo	96·0	88	Radium .	Ra	226·05
43	Masurium .	Ma	—	89	Actinium .	Ac	—
44	Ruthenium .	Ru	101·7	90	Thorium .	Th	232·12
45	Rhodium .	Rh	102·91	91	Protoactinium	Pa	231
46	Palladium .	Pd	106·7	92	Uranium	U	238·07

ANSWERS TO NUMERICAL EXAMPLES

Chapter I.—Pp. 50–51.

9. (*a*) It is a metal; hence Dulong and Petit's Law holds.
 (*b*) Rough value for atomic weight is 53·79.
 (*c*) Equivalent is 18·61; hence valency is 3, and correct atomic weight is 55·83.
 (*d*) Equivalent is 27·92; hence valency is 2, and correct atomic weight is 55·84.
10. 126·918; 126·920; 126·917.
11. 138·923; 138·909; 138·931.
12. 176·1.
13. 123·7.
14. Ag_2S : 2Ag = 1·158617; 1·148620; 1·148617; 1·148622.
 At. weight = 32·066; 32·066; 32·066; 32·067.
15. Common, 207·222; 207·209.
 Kolm, 205·990; 205·999.
 Uraninite, 206·194; 206·196.

Chapter V.—Pp. 215–216.

6. 27·880; 11·88.
7. (*a*) Ethylene, 28·051; (*b*) carbon dioxide, 44·014; (*c*) nitrous oxide 44·016; (*d*) sulphur dioxide, 64·004; (*e*) dimethyl ether 64·003.
 Atomic weights: Carbon (from *a*), 12·010; (from *b*), 12·014; (from *e*), 11·98; Nitrogen (from *c*), 14·008; Sulphur (from *d*) 32·00.

Chapter VI.—P. 278.

8. 630.
9. Ethylene, 101·2; Acetone, 160·2; Nitrosyl chloride, 110·0.
10. SF_6, 143·1; SeF_6, 159·8; TeF_6, 173·4.
11. The constant obtained by Dunstan's equation is 116·3. Hence the liquid is probably associated.
12. The value of the constant from Dunstan's equation is about 200, which would indicate that the liquid is probably associated. It should be noted, however, that nitrobenzene often behaves in an anomalous manner (*e.g.*, dielectric constant, p. 257), and hence it is unwise to place too much reliance on this figure.

Chapter VIII.—Pp. 379–381.

4. 136·1.
5. 97·59 per cent. of the sulphur dioxide is converted into the trioxide.

6. From observations at 1811° Abs., and 1877° Abs., 13,490 gm.-cals. are absorbed per gm.-mol. of NO. Using the data given for temperatures of 2580° Abs. and 2675° Abs. the value is 13,060 gm.-cals. per gm.-mol.

3·29 per cent. of the oxygen employed is converted into nitric oxide.

13. The reaction is unimolecular.
14. The reaction is unimolecular ($k = 0{\cdot}01148$).
16. 24,700 gm.-cals.
17. 58,500 gm.-cals.
18. The reaction is bimolecular ($k \times 10^3 = 2{\cdot}85, 2{\cdot}88, 2{\cdot}91, 2{\cdot}92$).
19. The reaction is bimolecular; using the equation

$$k = \frac{1}{(a-b)t}\log_e\frac{b(a-x)}{a(b-x)},\ k \times 10^4 = 4{\cdot}28,\ 4{\cdot}32,\ 4{\cdot}33,\ 4{\cdot}39,\ 4{\cdot}40.$$

Chapter X.—Pp. 464–465.

9. 97·3° C.

Chapter XI.—Pp. 502–504.

1. 10·75.
5. 296.
9. 132.
10. Nitrobenzene, 122; Benzoic acid, 107; Acetamide, 58; Atropine, 275; Vanillin, 130.
11. 251·9.
12. 29·56° C.; 161·1.
13. 210·9.
14. 101·4.
15. Caffeine, 207; Morphine, 289.
16. 624.
17. 170·5; 179·5; 189·1.

Chapter XII.—Pp. 537–538.

9. 2·241 atmos. at 0° C. (using $R = 0{\cdot}0821$ litre-atmos. per degree).
10. 0·91.
11. Ag^+, 0·431; NO_3^-, 0·569.
12. 0·005825 mhos.
15. Ag^+, 0·478; NO_3^-, 0·522.
16. 110·24; 117·6; 135·7.

Chapter XIII.—Pp. 583–584.

7. (*a*) 4·05; (*b*) 5·16; (*c*) 6·20.
8. $K_h = 3{\cdot}177 \times 10^{-5}$; $6{\cdot}674 \times 10^{-5}$; $3{\cdot}74 \times 10^{-4}$. The degree of hydrolysis, h, corresponding to the above hydrolysis constants is

$$5{\cdot}64 \times 10^{-3};\ 8{\cdot}17 \times 10^{-3};\ 1{\cdot}93 \times 10^{-2}.$$

The values of h given, have been calculated by neglecting h in comparison with unity.

9. Using the data for 18° C. and 100° C., the heat of ionisation of acetic acid is 638·7 gm.-cals.; and for ammonium hydroxide, 13,130 gm.-cals.

10. Distribution coefficient :—121, 119, 115, 121. **Mean, 119.**
$K_h \times 10^3$:—2·83, 2·53, 2·76, 2·70. **Mean, 2·71.**
$K_b \times 10^{11}$:—0·371.

Chapter XV.—Pp. 621–622.

1. 102,380 gm.-cals.
4. 323,300 gm.-cals.
8. 18,300 gm.-cals.
9. Constant pressure :—Ethane, 23,550 gm.-cals. Ethylene, − 7,830 gm.-cals. Acetylene, − 52,860 gm.-cals.
   Constant volume :—Ethane, 22,390 gm.-cals. Ethylene, − 8,410 gm.-cals. Acetylene, − 52,860 gm.-cals.

LOGARITHMS OF NUMBERS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 4	8 8	12 13	16 17	20 21	24 25	28 30	32 34	36 38
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 4	7 8	11 12	15 15	18 19	22 23	26 27	30 31	33 35
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 4	7 7	10 11	14 14	17 18	20 21	24 25	27 28	31 32
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 3	6 7	9 10	13 13	16 16	19 20	22 23	25 26	29 30
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 3	6 6	9 9	12 12	15 15	18 18	21 21	24 24	27 27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 3	6 6	8 9	11 11	14 14	17 17	19 20	22 23	25 26
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 3	5 5	8 8	10 11	13 13	15 16	18 19	21 21	23 24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2 3	5 5	7 8	10 10	12 13	15 15	17 18	20 20	22 23
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 2	5 5	7 7	9 10	12 12	14 14	16 17	19 19	21 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 2	4 5	7 7	9 9	11 11	13 14	16 16	18 18	20 20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

From Gibbs & Richards' Mathematical Tables by permission of Messrs. Christophers.

LOGARITHMS OF NUMBERS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	[illegible]	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

INDEX

The names of persons are given in italics, except where the name is an integral part of the reference. The numbers refer to pages.